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(71)Applicant : NISSAN MOTOR CO LTD

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(72)Inventor : YAMAMOTO SHINJI
TAKATANI SHINKO
TSUZUKI MIKIO

(54) EXHAUST GAS PURIFYING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To improve durability compared with the conventional catalyst and to exhibit excellent low temp. activity and purification efficiency, particularly excellent HC purification efficiency particularly after high temp. endurance at the time of purifying a low temp. exhaust gas.

SOLUTION: At the time of purifying the low temp. exhaust gas, a catalyst containing an oxygen adsorbent having oxygen storing ability selectively separating and adsorbing oxygen from the exhaust gas at a temp ranging from room temp. to 200° C and having oxygen releasing ability at a temp. ranging from 200-400° C is arranged at the upstream side to the exhaust gas flow, a catalyst containing a hydrocarbon adsorbent having hydrocarbon adsorbing ability at a temp. ranging from room temp. to 150° C and having hydrocarbon releasing and purifying ability at 150° C and a noble metal is arranged at the downstream side, a valve capable of switching an exhaust gas flow passage is arranged at the more upstream side of the catalyst arranged at the upstream side, the arrangement of the catalysts are set so as to supply oxygen through the upstream side catalyst to the downstream side catalyst when the catalyst arranged at the downstream side releases and purifies hydrocarbon at a catalytic temp. of 150-300° C and the valve is controlled corresponding to the temp. of the catalytic layer of the upstream side catalyst.

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JAPANESE

[JP,2000-042368,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS
EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1] In purifying low-temperature exhaust gas, exhaust gas flow is received. To the upstream The catalyst for which catalyst bed temperature contains the oxygen adsorption material which has the oxygen storage ability which dissociates and adsorbs the oxygen out of exhaust gas alternatively from a room temperature in a 200-degree C temperature region, and has oxygen emission ability in a 200 degrees C - 400 degrees C temperature region is arranged. The catalyst containing the hydrocarbon adsorption material which has hydrocarbon adsorption capacity from a room temperature in the downstream in a 150-degree C temperature region, and has hydrocarbon desorption and decontamination capacity in a 150-degree C temperature region, and noble metals is arranged. The bulb of the catalyst arranged to said upstream in which the exhaust gas passage switch to the upstream is still more possible is arranged. In case the catalyst arranged to this downstream ****s and purifies a hydrocarbon in a temperature region with a catalyst bed temperature [the] of 150 degrees C - 300 degrees C It is the exhaust gas purification approach which the above-mentioned catalyst arrangement is set up so that oxygen may be supplied to the catalyst of the downstream from the catalyst of this upstream, and is characterized by adjusting said bulb according to the temperature in the catalyst bed of the catalyst of the upstream.

[Claim 2] The catalyst arranged to the upstream is SiO₂ / aluminum 2O₃ as oxygen adsorption material. The exhaust gas purification approach according to claim 1 characterized by a ratio containing 20 or less A mold and X zeolite.

[Claim 3] The exhaust gas purification approach according to claim 1 or 2 characterized by preventing flowing into the catalyst to which the bulb installed in the upstream of this catalyst was operated, exhaust gas passage was changed, and exhaust gas has arranged the temperature of 400 degrees C or more to the upstream concerned when the temperature in the catalyst bed of the catalyst arranged to the upstream reaches 400 degrees C.

[Claim 4] The catalyst arranged to the upstream is the next empirical formula: [A] [B] O_y (it La(s) among a formula A). The element more than a kind chosen from the group which consists of Sr, Ba, Pb, Nd, and Ce, The element more than a kind chosen from the group which B becomes from aluminum, Ti, Cr, Mn, Co, Fe, and nickel, an oxygen atomic number required for O to show oxygen and for y satisfy the valence of each element — being shown — claims 1-3 characterized by containing the multiple oxide of the perovskite type structure expressed — the exhaust gas purification approach given [one of] in a term.

[Claim 5] The catalyst arranged to the upstream is the exhaust gas purification approach according to claim 1 to 4 characterized by containing the cerium oxide which supported platinum and/or palladium.

[Claim 6] The catalyst arranged to the downstream is the exhaust gas purification approach according to claim 1 to 5 characterized by containing the zeolite more than a kind chosen from the group which consists of ZSM5, USY, and a beta-zeolite as hydrocarbon adsorption material, the metal more than a kind chosen from the group which consists of platinum, palladium, and a rhodium as noble metals, an activated alumina, Seria oxide, a zirconic acid ghost, and a barium compound.

[Claim 7] Hydrocarbon adsorption material is the exhaust gas purification approach according to claim 6 characterized by containing the element more than a kind chosen from the group which consists of platinum, palladium, Lynn, boron, magnesium, and calcium.

[Claim 8] the element more than a kind chosen from the group which becomes the upper part of a hydrocarbon adsorption material layer from palladium, a zirconium and neodium, and a lanthanum — metal conversion — 1-40-mol % and a cerium — 60-98-mol % — the exhaust gas purification approach according to claim 6 or 7 characterized by arranging the catalyst component layer containing the included cerium oxide.

[Claim 9] The exhaust gas purification approach according to claim 8 further characterized by arranging the catalyst component layer containing the zirconic acid ghost which contains a 1-30 mol % zirconium for the element more than a kind chosen from the group which consists of platinum, a rhodium, a cerium, neodium, and a lanthanum 70 to 98% by metal conversion, and an activated alumina in the upper part of the catalyst component layer containing the palladium arranged in the upper part of a hydrocarbon adsorption material layer.

[Claim 10] The exhaust gas purification approach according to claim 8 or 9 characterized by arranging the three way component catalyst which was chosen from the group which becomes the upper part of a hydrocarbon adsorption material layer from alkali metal and alkaline earth metal, and which a kind contains at least.

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DETAILED DESCRIPTION

Detailed Description of the Invention]

[0001]

Field of the Invention] Especially this invention relates to the exhaust gas purification approach which can purify HC efficiently especially among the hydrocarbon in the exhaust gas discharged from internal combustion engines, such as an automobile, at the time of the low temperature immediately after engine starting ("HC" is called hereafter), a carbon monoxide ("CO" is called below), and a nitriding oxide ("NOx" is called hereafter) about the exhaust gas purification approach.

[0002]

Description of the Prior Art] the approach of desorb, after use HC adsorption material, store temporarily for the purpose of reduction of the hydrocarbon in the exhaust gas discharge at the time of the low temperature immediately after engine starting ("cold HC" be called hereafter) and activate a three way component catalyst from before, since the catalyst for exhaust gas purification do not have the enough endurance under an elevated temperature, a catalyst deteriorate and decontamination capacity fall remarkably, and purify with this three way component catalyst be examine.

[0003] As a catalyst for exhaust gas purification using this HC adsorption material, there are some which are indicated by JP,6-74019,A, JP,7-144119,A, JP,6-142457,A, JP,5-59942,A, or JP,7-102957,A, for example.

[0004] After establishing bypass passage in exhaust air passage, making JP,6-74019,A once stick to HC adsorption material which has arranged HC discharged at the time of cold one immediately after engine starting to bypass passage, switching exhaust air passage to it after that and activating a down-stream three way component catalyst, the system which purifies gradually HC desorbed through HC adsorption catalyst from a part of exhaust gas with a latter three way component catalyst is proposed.

[0005] In JP,7-144119,A, heat is taken by the three way component catalyst of the preceding paragraph at the time of cold one immediately after engine starting, the adsorption effectiveness of HC adsorption material of the middle is raised, and the system which makes heat transfer of the heat of reaction easy to carry out to a latter three way component catalyst through HC adsorption material of the middle which carried out tandem arrangement in after three way component catalyst activation of the preceding paragraph, and promotes purification with a latter three way component catalyst is proposed.

[0006] In case HC to which it stuck in the low-temperature region ****s, the preheating of the exhaust gas including Desorption HC is carried out by the heat exchanger, and the cold HC adsorption treatment system which promotes purification with a three way component catalyst is proposed by JP,6-142457,A.

[0007] By switching the passage of the exhaust gas by catalyst arrangement and the bulb, the temperature up of HC adsorption material is made slow, and the system which improves the adsorption effectiveness of cold HC is proposed by JP,5-59942,A.

[0008] Moreover, in order to improve the purification engine performance of a latter oxidation and three way component catalyst, air is supplied between the three way component catalyst of the preceding paragraph, and HC adsorption material of the middle, and the system which promotes activation of a latter oxidation and three way component catalyst is proposed by JP,7-102957,A.

[0009]

[Problem(s) to be Solved by the Invention] However, HC adsorption effectiveness falls after durability, moreover, since the conventional system using HC adsorption material indicated in said official report of the endurance of HC adsorption material is inadequate, before a latter three way component catalyst is activated, HC will ***** and emission will be worsened in it.

[0010] Then, in order to attain improvement in adsorption effectiveness and the formation of desorption delay of HC adsorption material, the heat exchanger for the method of bypassing elevated-temperature gas or three way component catalyst pre-heating is used, but while a system configuration makes it complicated, sufficient effectiveness is not acquired, but since cost goes up remarkably, moreover, HC adsorption material with high endurance and adsorption effectiveness is desired.

[0011] In order to use noble metals so much in order to maintain the high purification engine performance from the first stage to until after durability, or to aim at promotion of purification of early activation and Desorption HC, especially the three way component catalyst aiming at purification of HC desorbed from HC adsorption material introduces air, and is shining and carrying out it. For this reason, although a catalyst from which the purification engine performance in which the amount of noble metals to be used is high at least is obtained was desired, when noble metals were reduced, endurance became inadequate and after durability had the problem that the catalytic activity and the purification engine performance in a low-temperature region got worse.

[0012] Therefore, in purifying low-temperature exhaust gas, the purpose of this invention is to offer the exhaust gas purification approach which shows the low-temperature activity and the purification engine performance which endurance improved and the conventional catalyst was excelled especially after elevated-temperature durability, and HC purification effectiveness in which it excelled especially.

[0013]

[Means for Solving the Problem] In purification of the low-temperature exhaust gas immediately after engine starting discharged by the internal combustion engine as a result of inquiring, in order that this invention persons may solve the above-mentioned technical

problem The catalyst which has hydrocarbon adsorption and decontamination capacity for the catalyst which has oxygen storage / emission ability in the upstream of exhaust gas in the downstream is arranged. When the catalyst of the downstream ***** and purified a hydrocarbon, HC purification effectiveness at the time of cold HC to which it stuck ***** reached [being improved and maintained remarkably and] a header and this invention by supplying oxygen to the catalyst of the downstream from the catalyst of the upstream.

[0014] In the exhaust gas purification approach according to claim 1 purifying low-temperature exhaust gas The catalyst containing the oxygen adsorption material to which catalyst bed temperature has the oxygen storage ability which dissociates and adsorbs the oxygen out of exhaust gas alternatively from a room temperature in the upstream in a 200-degree C temperature region, and has oxygen emission ability in it in a 200 degrees C - 400 degrees C temperature region is arranged to exhaust gas flow. The catalyst containing the hydrocarbon adsorption material which has hydrocarbon adsorption capacity from a room temperature in the downstream in a 150-degree C temperature region, and has hydrocarbon desorption and decontamination capacity in a 150-degree C temperature region, and noble metals is arranged. The bulb of the catalyst arranged to said upstream in which the exhaust gas passage switch to the upstream is still more possible is arranged. In case the catalyst arranged to this downstream ***** and purifies a hydrocarbon in a temperature region with a catalyst bed temperature [the] of 150 degrees C - 300 degrees C The above-mentioned catalyst arrangement is set up so that oxygen may be supplied to the catalyst of the downstream from the catalyst of this upstream, and it is characterized by adjusting said bulb according to the temperature in the catalyst bed of the catalyst of the upstream.

[0015] For the exhaust gas purification approach according to claim 2, the catalyst arranged to the upstream in the exhaust gas purification approach according to claim 1 is SiO₂ / aluminum 2O₃ as oxygen adsorption material. It is characterized by a ratio containing 20 or less A mold and X zeolite.

[0016] The exhaust gas purification approach according to claim 3 is characterized by preventing flowing into the catalyst to which the bulb installed in the upstream of this catalyst was operated, exhaust gas passage was changed, and exhaust gas has arranged the temperature of 400 degrees C or more to the upstream concerned, when the temperature in the catalyst bed of the catalyst arranged to the upstream reaches 400 degrees C in the exhaust gas purification approach according to claim 1 or 2.

[0017] In the exhaust gas purification approach given [one of] in a term the exhaust gas purification approach according to claim 4 — claims 1-3 — the catalyst arranged to the upstream — the next empirical formula: [A] [B] O_y (the element more than a kind chosen from the group which A becomes from La, Sr, Ba, Pb, Nd, and Ce among a formula, and B) an oxygen atomic number required for the element more than a kind chosen from the group which consists of aluminum, Ti, Cr, Mn, Co, Fe, and nickel, and O to show oxygen, and for y satisfy the valence of each element — being shown — it is characterized by containing the multiple oxide of the perovskite type structure expressed.

[0018] the exhaust gas purification approach according to claim 5 — claims 1-4 — in the exhaust gas purification approach given [one of] in a term, the catalyst arranged to the upstream is characterized by containing the cerium oxide which supported platinum and/or palladium.

[0019] In the exhaust gas purification approach given [one of] in a term the exhaust gas purification approach according to claim 6 — claims 1-5 — The zeolite more than a kind chosen from the group which the catalyst arranged to the downstream becomes from ZSM5, USY, and beta-zeolite as hydrocarbon adsorption material. It is characterized by containing the metal more than a kind chosen from the group which consists of platinum, palladium, and a rhodium as noble metals, an activated alumina, Seria oxide, a zirconic acid ghost, and a barium compound.

[0020] The exhaust gas purification approach according to claim 7 is characterized by hydrocarbon adsorption material containing the element more than a kind chosen from the group which consists of platinum, palladium, Lynn, boron, magnesium, and calcium in the exhaust gas purification approach according to claim 6.

[0021] the element more than a kind chosen from the group to which the exhaust gas purification approach according to claim 8 becomes the upper part of a hydrocarbon adsorption material layer from palladium, a zirconium and neodium, and a lanthanum in the exhaust gas purification approach according to claim 7 — metal conversion — 1-40-mol % and a cerium — 60-98-mol % — it is characterized by arranging the catalyst component layer containing the included cerium oxide.

[0022] The exhaust gas purification approach according to claim 9 is set to the exhaust gas purification approach according to claim 8. In the upper part of the catalyst component layer containing the palladium arranged in the upper part of a hydrocarbon adsorption material layer Furthermore, the zirconic acid ghost which contains a 1-30 mol % zirconium for a kind chosen from the group which consists of platinum, a rhodium, a cerium, neodium, and a lanthanum 70 to 98% by metal conversion, The exhaust gas purification approach according to claim 8 characterized by arranging the catalyst component layer containing an activated alumina.

[0023] The exhaust gas purification approach according to claim 10 is characterized by arranging the three way component catalyst which was chosen from the group which becomes the upper part of a hydrocarbon adsorption material layer from alkali metal and alkaline earth metal and which a kind contains at least in the exhaust gas purification approach according to claim 8 or 9.

[0024]

[Embodiment of the Invention] In purifying the low-temperature exhaust gas immediately after engine starting discharged by the internal combustion engine as the exhaust gas purification approach of this invention The catalyst containing the oxygen adsorption material to which catalyst bed temperature has the oxygen storage ability which dissociates and adsorbs the oxygen out of exhaust gas alternatively from a room temperature in the upstream in a 200-degree C temperature region, and has oxygen emission ability in it in a 200 degrees C - 400 degrees C temperature region is arranged to exhaust gas flow. The catalyst containing the hydrocarbon adsorption material which has hydrocarbon adsorption capacity from a room temperature in the downstream in a 150-degree C temperature region, and has hydrocarbon desorption and decontamination capacity in a 150-degree C temperature region, and noble metals is arranged. The bulb of the catalyst arranged to said upstream in which the exhaust gas passage switch to the upstream is still more possible is arranged. In case the catalyst arranged to this downstream ***** and purifies a hydrocarbon in a temperature region with a catalyst bed temperature [the] of 150 degrees C - 300 degrees C The above-mentioned catalyst arrangement is set up so that oxygen may be supplied to the catalyst of the downstream from the catalyst of this upstream, and said bulb can improve the

desorption hydrocarbon purification effectiveness of the catalyst of this downstream by considering as the configuration adjusted according to the temperature in the catalyst bed of the catalyst of the upstream.

[0025] The oxygen adsorption material ingredient which has oxygen storage / supply ability which the catalyst arranged to the upstream contains is SiO₂ / aluminum 2O₃ which can dissociate and adsorb oxygen alternatively out of low-temperature exhaust gas. 20 or less A mold and an X type zeolite have an effective ratio. Catalyst bed temperature separates and stores the oxygen in exhaust gas alternatively from a room temperature in a 200-degree C temperature region, and can emit oxygen in a 200 to 400 degrees C temperature region, the catalyst which made this zeolite contain can supply oxygen efficiently, in case the catalyst of the downstream purifies and purifies the hydrocarbon to which it stuck from low-temperature exhaust gas, and it can raise HC purification effectiveness of noble metals. As for the amount, per [catalyst 1L / 10g-300g] are desirable from the point of the improvement in the engine performance.

[0026] Moreover, although the bulb installed in the upstream of this catalyst is operated and exhaust gas passage is changed when the temperature in the catalyst bed of this upstream (a thermometric element is installed into the catalyst bed concerned, and temperature is detected) reaches 400 degrees C, this is for preventing that exhaust gas with a temperature of 400 degrees C or more flows into oxygen adsorption material, and preventing the structure destruction by the heat of this zeolite.

[0027] moreover — as the ingredient which was excellent in thermal resistance in order that the catalyst arranged to this upstream might emit oxygen by the rise of catalyst bed temperature in a temperature region 200 degrees C or more — the next empirical formula: [A] [B] Oy (A) The element more than a kind chosen from the group which consists of La, Sr, Ba, Pb, Nd, and Ce, and B an oxygen atomic number required for the element more than a kind chosen from the group which consists of Al, Ti, Cr, Mn, Co, Fe, and Ni, and O to show oxygen, and for y satisfy the valence of each element — being shown — the multiple oxide of the oxygen migratory high perovskite type structure expressed can be contained. By this, the degradation of the oxygen adsorption material slack zeolite arranged to this upstream can be compensated, and the purification effectiveness of the desorption hydrocarbon of the catalyst arranged to this downstream can be improved further.

[0028] Furthermore, since the catalyst arranged to this upstream promotes the operation which emits oxygen by the rise of catalyst bed temperature in a temperature region 200 degrees C or more, the cerium oxide which supported platinum and/or palladium can be made to contain. By making this catalyst contain platinum and/or a palladium support cerium oxide, the endurance of the catalyst arranged to the upstream improves and the purification effectiveness of the desorption hydrocarbon of the catalyst arranged to this downstream can be improved over a long period of time.

[0029] As amount of the sum total used of the ingredient which has oxygen storage / supply ability which the catalyst arranged to the upstream contains, they are the above, and SiO₂ / aluminum 2O₃. Per [upper catalyst 1L / 10g-300g] are desirable combining the cerium oxide with which the ratio supported 20 or less A mold and an X type zeolite, the multiple oxide of perovskite type structure, and platinum and/or palladium. The adsorption engine performance is saturated with less than 10g, and the amount of the ingredient used which has oxygen storage / supply ability is not economically effective at it, even if the adsorption engine performance is not fully discovered and exceeds 300g conversely.

[0030] Moreover, as an ingredient which adsorbs the hydrocarbon discharged in the low-temperature region arranged at the downstream, they are SiO₂ / aluminum 2O₃. The various hydrocarbons discharged in a low-temperature region can be efficiently adsorbed by using more than a kind chosen from the group which a ratio becomes from 20 or more ZSM5, USY(s), and beta-zeolites. As for the amount of the hydrocarbon adsorption material used, per [catalyst 1L / 10g-300g] are desirable. The adsorption engine performance is saturated with less than 10g, and the amount of the hydrocarbon adsorption material used is not economically effective at it, even if the adsorption engine performance is not fully discovered and exceeds 300g conversely. Furthermore, since the hydrocarbon desorbed from this hydrocarbon adsorption material is purified, the hydrocarbon from which it is desorbed with the rise of catalyst bed temperature can be efficiently purified by containing the element more than a kind chosen from the group which consists of platinum, palladium, and a rhodium as noble metals, an activated alumina, Seria oxide, a zirconic acid ghost, and a barium compound. 1g-30g, and an activated alumina are [10g-300g, and Seria oxide / 5g-100g, and a zirconic acid ghost / 5g-100g, and a barium compound] desirable [the amount / per / catalyst 1L / and noble metals / that they are 1g-50g] from the point which purifies Desorption HC efficiently.

[0031] Furthermore, since the structural stability under the elevated temperature of hydrocarbon adsorption material (thermal resistance), adsorption capacity cold [HC], and HC desorption control engine performance at the time of a temperature rise are improved, the element more than a kind chosen from the group which consists of platinum, palladium, Lynn, boron, magnesium, and calcium can be contained. The content of this element is 10 % of the weight from 0.1 % of the weight to HC adsorption material. If it is less than 0.1 % of the weight, sufficient amelioration effectiveness will not be acquired, but if it is conversely used mostly from 10 % of the weight, the pore of a zeolite will blockade and HC adsorption capacity will fall.

[0032] furthermore, the element more than a kind chosen from the group which becomes the upper part of this hydrocarbon adsorption material layer from palladium, a zirconium and neodium, and a lanthanum in order to improve the purification effectiveness at the time of HC to which it stuck by hydrocarbon adsorption material — metal conversion — a 1-40 mol % cerium — 60-98-mol % — the catalyst component layer containing the included cerium oxide can be arranged. In order to raise the purification engine performance and endurance of palladium especially, in a palladium content catalyst component layer the element more than a kind chosen from the group which consists of a zirconium, neodium, and a lanthanum — metal conversion — a 1-40 mol % cerium — 60-98-mol % — by making the included cerium oxide contain Since the high cerium oxide of oxygen occlusion ability becomes easy to emit grid oxygen and adsorption oxygen a rich ambient atmosphere and near SUTOIKI, it should be suitable for purification of exhaust gas in the oxidization condition of palladium, and the fall of the catalyst ability of palladium can be controlled. As for the amount of this palladium used, it is desirable from the point of the purification engine performance that they are per [catalyst 1L / 1g-30g]. The amount of this cerium oxide used is per [catalyst 1L / 5-100g]. The amelioration effectiveness saturates and is not effective, even if the dispersibility of sufficient noble metals will not be acquired but it will use it mostly from 100g, if it is less than 5g.

[0033] furthermore, the element more than a kind chosen from the group which becomes the upper part of the catalyst component

ayer containing palladium from platinum, a rhodium, a cerium, neodium, and a lanthanum in order to improve the poisoning-proof nature and the purification engine performance of palladium — metal conversion — a 1–30 mol % zirconium — 70–98-mol % — the catalyst component layer containing the included zirconic acid ghost and an activated alumina can be arranged. As a base material with which said platinum and rhodium are supported, in order to raise the endurance of platinum or a rhodium, a zirconic acid ghost is suitable. Since the high cerium content zirconic acid ghost of oxygen occlusion ability especially becomes easy to emit grid oxygen and adsorption oxygen a rich ambient atmosphere and near SUTOIKI, it should be suitable for purification of exhaust gas in the oxidation condition of platinum or a rhodium, and the fall of the catalyst ability of platinum or a rhodium can be controlled.

[0034] The cerium content of this zirconic acid ghost is 0.01–mol % to 30–mol %. Less than [0.01 mol %], a cerium content is ZrO_2 . ZrO_2 of the element which was not different from a case and was described above. If the amelioration effectiveness by the oxygen occlusion ability of a cerium does not show up and a cerium content exceeds 30–mol %, a BET specific surface area and thermal stability will fall [this effectiveness] to saturation or reverse. The amount of the zirconic acid ghost used is per [catalyst 1L / 5–100g]. The amelioration effectiveness saturates and is not effective, even if the dispersibility of sufficient noble metals will not be acquired but it will use it mostly from 100g, if it is less than 5g.

[0035] Moreover, since the low-temperature activity of palladium is improved, the three way component catalyst containing alkali metal and/or alkaline earth metal can be arranged. There are a potassium, calcium, strontium, barium, sodium, magnesium, an yttrium, a lanthanum, etc. in these metals. The content of this element is among [1–40g] catalyst 1L. In less than 1g, neither relaxation of adsorption poisoning to the noble metals of HC nor sintering of palladium can be controlled, but even if it exceeds 40g, the capable increase-in-quantity effectiveness is not acquired, but the engine performance is reduced conversely.

[0036]

[Example] The example of preparation, a following example, and the following example of a comparison explain this invention. The section is weight ***** as long as there is especially no display.

[0037] A mold zeolite powder of example of preparation $1\text{SiO}_2/\text{aluminum}_2\text{O}_3 = 15$ The 400 sections, Empirical formula: $[\text{La}_{0.6}\text{Sr}_{0.3}\text{Ba}_{0.1}]$ and $[\text{Mn}_{0.4}\text{Co}_{0.4}\text{Fe}_{0.1}\text{aluminum}_{0.1}]$ Oy Perovskite mold multiple oxide powder The 250 sections, The palladium support cerium oxide ($\text{La}_{0.01}\text{Zr}_{0.32}\text{Ce}_{0.67}\text{O}_x$) powder of 0.1% of palladium support concentration The 250 sections, With the 500 sections, 2000g of pure water was fed into the magnetic ball mill, the silica sol (SiO_2 as concentration 20%) was mixed and ground, and the slurry was obtained. This slurry liquid was made to adhere to the nature monolith support of cordierite (1.0L, 400 cels), the slurry of the surplus in a cel was removed and dried in airstream, and it calcinated at 400 degrees C for 1 hour. This activity was done twice and the upper catalyst A of amount weight of coats 300 g/L–support was acquired. The amount of palladium support was 2.12 g/cf (0.075 g/L).

[0038] The 200 sections and USY of $\text{SiO}_2/\text{aluminum}_2\text{O}_3 = 25$ for the 600 sections and ZSM5 of $\text{SiO}_2/\text{aluminum}_2\text{O}_3 = 50$ The 100 sections, [beta-zeolite powder of example of preparation $2\text{SiO}_2/\text{aluminum}_2\text{O}_3 = 25$] With the 500 sections, 1500g of pure water was fed into the magnetic ball mill, the silica sol (SiO_2 as concentration 20%) was mixed and ground, and the slurry was obtained. This slurry liquid was made to adhere to the nature monolith support of cordierite (1.0L, 400 cels), the slurry of the surplus in a cel was removed and dried in airstream, and it calcinated at 400 degrees C for 1 hour. This activity was done twice and the upper catalyst of amount weight of coats 200 g/L–support was acquired (catalyst B).

[0039] After sinking the palladium nitrate water solution into the alumina powder (powder A) containing cerium 3 mol % (it converts into CeO_2 and is 8.7 % of the weight), zirconium 3 mol % (it converts into ZrO_2 and is 6.3 % of the weight), and lanthanum 2 mol % (it converts into La_2O_3 , and is 5.5 % of the weight) and drying at 150 degrees C for 12 hours, it calcinated at 400 degrees C for 1 hour, and Pd support alumina powder (powder B) was obtained. Pd concentration of this powder B was 11 % of the weight.

[0040] After sinking the palladium nitrate water solution into the cerium oxide powder (powder C) containing lanthanum 1 mol % (it converts into La_2O_3 , and is 2 % of the weight), and zirconium 32 mol % (it converts into ZrO_2 and is 25 % of the weight) and drying at 150 degrees C for 12 hours, it calcinated at 400 degrees C for 1 hour, and Pd support cerium oxide ($\text{La}_{0.01}\text{Zr}_{0.32}\text{Ce}_{0.67}\text{O}_x$) powder (powder D) was obtained. Pd concentration of this powder D was 2.5 % of the weight.

[0041] The above-mentioned powder B880g, powder D280g, 40g of activated aluminas, and 1500g of nitric-acid water solutions were fed into the magnetic ball mill, they were mixed and ground, and the slurry was obtained. This slurry liquid was made to adhere to Catalyst B, the slurry of the surplus in a cel was removed and dried in airstream, and it calcinated at 400 degrees C for 1 hour. This activity was done twice and the catalyst of the amount weight of coats of 260g / L–support was acquired. The amount of palladium support was 146.67 g/cf (5.18 g/L) (catalyst C).

[0042] Subsequently, after sinking a nitric-acid rhodium water solution into the activated-alumina object powder (powder E) which supported 3 % of the weight of Zr and drying at 150 degrees C for 12 hours, it calcinates at 400 degrees C for 1 hour, and it is 3 % of the weight-aluminum 2O_3 of Rh support Zr. Powder (powder F) was obtained. Rh concentration of this powder F was 2.0 % of the weight.

[0043] The 300 sections, the activated-alumina 30 section, and 1500g of nitric-acid water solutions were fed into the magnetic ball mill for the 470 sections and zirconic acid ghost powder (La_1 mol %, Ce_{20} mol %, and Zr_{79} mol %) (powder F), the above-mentioned powder E was mixed and ground, and the slurry was obtained. This slurry liquid was made to adhere to Catalyst C, the slurry of the surplus in a cel was removed and dried in airstream, and it calcinated at 400 degrees C for 1 hour. This activity was done twice and the catalyst of the amount weight of coats of 300g / L–support was acquired. The amount of rhodium support was 13.33 g/cf (0.47 g/L) (catalyst D).

[0044] E Subsequently, after making a barium acetate solution adhere to the above-mentioned nature monolith support of catalyst component support cordierite, calcinated at 400 degrees C for 1 hour, 10 g/L was made to contain as BaO , and the down-stream catalyst was acquired.

[0045] In the A mold zeolite powder 400 section of example of preparation $3\text{SiO}_2/\text{aluminum}_2\text{O}_3 = 15$, instead of, The X type zeolite powder of $\text{SiO}_2/\text{aluminum}_2\text{O}_3 = 15$ is made into the 400 sections. Empirical formula: $[\text{La}_{0.6}\text{Sr}_{0.3}\text{Ba}_{0.1}]$ and $[\text{Mn}_{0.4}\text{Co}_{0.4}\text{Fe}_{0.1}\text{aluminum}_{0.1}]$ Oy In the perovskite mold multiple oxide powder 250 section, instead of, An empirical formula $[\text{La}_{0.5}\text{Sr}_{0.2}\text{Ba}_{0.2}\text{Ce}_{0.05}\text{Nd}_{0.05}]$ and $[\text{Cr}_{0.1}\text{Mn}_{0.3}\text{Fe}_{0.1}\text{nickel}_{0.1}\text{aluminum}_{0.05}\text{Ti}_{0.05}]$ The perovskite mold multiple oxide powder of Oy is made into the 250 sections. Except having used the amount of the platinum support cerium oxide ($\text{La}_{0.01}\text{Zr}_{0.32}\text{Ce}_{0.67}\text{O}_x$) powder of 0.1 % of the

weight of platinum support concentration as the 250 sections, the upper catalyst F was acquired according to the example 1.

0046] In the A mold zeolite powder 400 section of example of preparation 4SiO₂/aluminum₂O₃=15, instead of, The 100 sections and the X type zeolite powder of SiO₂/aluminum₂O₃=15 are made into the 100 sections for A mold zeolite powder of aluminum₂O₃/aluminum₂O₃=15. Empirical formula: [La_{0.6} Sr_{0.3} Ba_{0.1}] and [Mn_{0.4} Co_{0.4} Fe_{0.1} aluminum_{0.1}] Oy In the perovskite mold multiple oxide powder 250 section, instead of, An empirical formula [La_{0.5} Sr_{0.2} Ba_{0.2} Ce_{0.05} Nd_{0.05}] and [Cr_{0.1} Mn_{0.3} Fe_{0.1} nickel_{0.1} aluminum_{0.05} Ti_{0.05}] Oy Perovskite mold multiple oxide powder is made into the 100 sections. Except having used the amount of the palladium support cerium oxide (La_{0.01}Zr_{0.32}Ce_{0.67}O_x) powder of 0.1 % of the weight of palladium support concentration as the 600 sections, the upper catalyst G was acquired according to the example 1.

0047] In the A mold zeolite powder 400 section of example of preparation 5SiO₂/aluminum₂O₃=15, instead of, The 50 sections and the X type zeolite powder of SiO₂/aluminum₂O₃=15 are made into the 50 sections for A mold zeolite powder of SiO₂/aluminum₂O₃=15. Empirical formula: [La_{0.6} Sr_{0.3} Ba_{0.1}] and [Mn_{0.4} Co_{0.4} Fe_{0.1} aluminum_{0.1}] Oy In the perovskite mold multiple oxide powder 250 section, instead of, An empirical formula [La_{0.8} Sr_{0.1} Ba_{0.1}] and [Mn_{0.1} Co_{0.9}] Oy Perovskite mold multiple oxide powder is made into the 100 sections. Except having used the amount of the palladium support cerium oxide (La_{0.01}Zr_{0.32}Ce_{0.67}O_x) powder of 0.1 % of the weight of palladium support concentration as the 700 sections, the upper catalyst H was acquired according to the example 1.

0048] In the A mold zeolite powder 400 section of example of preparation 6SiO₂/aluminum₂O₃=15, instead of, A mold zeolite powder of SiO₂/aluminum₂O₃=15 is made into the 50 sections. Empirical formula: [La_{0.6} Sr_{0.3} Ba_{0.1}] and [Mn_{0.4} Co_{0.4} Fe_{0.1} aluminum_{0.1}] Oy In the perovskite mold multiple oxide powder 250 section, instead of, An empirical formula [La_{0.8} Sr_{0.1} Ba_{0.1}] and [Mn_{0.1} Co_{0.9}] Oy It considers as the perovskite mold multiple oxide powder 50 section. Except having used the amount of the palladium support cerium oxide (La_{0.01}Zr_{0.32}Ce_{0.67}O_x) powder of 0.1 % of the weight of palladium support concentration as the 900 sections, the upper catalyst I was acquired according to the example 1.

0049] In the A mold zeolite powder 400 section of example of preparation 7SiO₂/aluminum₂O₃=15, instead of, The X type zeolite powder of SiO₂/aluminum₂O₃=15 is made into the 50 sections. Empirical formula: [La_{0.6} Sr_{0.3} Ba_{0.1}] and [Mn_{0.4} Co_{0.4} Fe_{0.1} aluminum_{0.1}] Oy In the perovskite mold multiple oxide powder 250 section, instead of, Empirical formula [La_{0.9} Sr_{0.1}] Oy Perovskite mold multiple oxide powder is made into the 50 sections. Except having used the amount of the palladium support cerium oxide (La_{0.01}Zr_{0.32}Ce_{0.67}O_x) powder of 0.1 % of the weight of palladium support concentration as the 800 sections, the upper catalyst J was acquired according to the example 1.

0050] The beta-zeolite powder 600 section of example of preparation 8SiO₂/aluminum₂O₃=25, ZSM5 of SiO₂/aluminum₂O₃=50 In the 200 sections and the USY100 section of SiO₂/aluminum₂O₃=25, instead of, According to the example 2, the down-stream catalyst K was acquired except having used [the amount of beta-zeolite powder of SiO₂/aluminum₂O₃=25] the 50 sections and the amount of USY of SiO₂/aluminum₂O₃=25 for the 800 sections and the amount of ZSM5 of SiO₂/aluminum₂O₃=50 as the 50 sections.

0051] In the beta-zeolite powder 600 section of example of preparation 9SiO₂/aluminum₂O₃=25, instead of, According to the example 2, the down-stream catalyst L was further acquired except not using ZSM5 of SiO₂/aluminum₂O₃=50, and USY of SiO₂/aluminum₂O₃=25, using the amount of beta-zeolite powder of SiO₂/aluminum₂O₃=25 as the 900 sections.

0052] ZSM5 of example of preparation 10SiO₂/aluminum₂O₃=50 The 200 sections, The USY100 section of SiO₂/aluminum₂O₃=25 is replaced. ZSM5 of SiO₂/aluminum₂O₃=50 The 400 sections, According to the example 2, the down-stream catalyst M was acquired except not using beta-zeolite powder of SiO₂/aluminum₂O₃=25 further, using the amount of USY of SiO₂/aluminum₂O₃=25 as the 900 sections.

0053] According to the example 9, the down-stream catalyst N was acquired except having used the beta-zeolite 900 section of SiO₂/aluminum₂O₃=50 containing 0.5 % of the weight of boron, and 0.1 % of the weight of calcium instead of the beta-zeolite powder 900 section of example of preparation 11SiO₂/aluminum₂O₃=50.

0054] The beta-zeolite powder 600 section of example of preparation 12SiO₂/aluminum₂O₃=25, ZSM5 of SiO₂/aluminum₂O₃=50 In the 200 sections and the USY100 section of SiO₂/aluminum₂O₃=25, instead of, The beta-zeolite 700 section of SiO₂/aluminum₂O₃=25 containing 0.1 % of the weight of Linn, 0.1 % of the weight of magnesium, and 0.1 % of the weight of palladium, ZSM5 of SiO₂/aluminum₂O₃=50 containing 0.1 % of the weight of platinum, 0.1 % of the weight of boron, and 0.1 % of the weight of calcium The 100 sections, According to the example 9, the down-stream catalyst O was acquired except having used the USY100 section of SiO₂/aluminum₂O₃=25 containing 0.5 % of the weight of Linn, and 0.1 % of the weight of calcium.

0055] According to the example 1, the upper catalyst P was acquired except having used only the A mold zeolite powder 900 section of example of comparison preparation 1SiO₂/aluminum₂O₃=15, and the silica sol (SiO₂ as concentration 20%) 500 section.

0056] According to the example 1, the upper catalyst Q was acquired except having used only the example of comparison preparation 2[La_{0.6} Sr_{0.3} Ba_{0.1}] [Mn_{0.4} Co_{0.4} Fe_{0.1} aluminum_{0.1}] Oy powder 900 section, and the silica sol (SiO₂ as concentration 20%) 500 section.

0057] According to the example 1, the upper catalyst R was acquired except having used only the palladium support cerium oxide (La_{0.01}Zr_{0.32}Ce_{0.67}O_x) powder 900 section of 0.1 % of the weight of example of comparison preparation 3 palladium support concentration, and the silica sol (SiO₂ as concentration 20%) 500 section.

0058] Powder B880g and powder D280g which was obtained in the example of comparison preparation 4 example 2, and 40g of activated aluminas and 1500g of nitric-acid water solutions were fed into the magnetic ball mill, were mixed and ground, and the slurry was obtained. This slurry liquid was made to adhere to the nature monolith support of cordierite (1.0L, 400 cels), the slurry of the surplus in a cel was removed and dried in airstream, and it calcinated at 400 degrees C for 1 hour. This activity was done twice and the catalyst of the amount weight of coats of 60g / L-support was acquired. The amount of palladium support was 146.67 g/cf (5.18 g/L) (catalyst S).

0059] Subsequently, with the powder E470 section obtained in the example 2, the zirconic acid ghost powder (powder F) 300 section [La1 mol %, Ce20 mol %, and Zr79 mol %], and the activated-alumina 30 section, 1500g of nitric-acid water solutions was fed into the magnetic ball mill, they were mixed and ground, and the slurry was obtained. This slurry liquid was made to adhere to the above-

mentioned catalyst S, the slurry of the surplus in a cel was removed and dried in airstream, and it calcinated at 400 degrees C for 1 hour. This activity was done twice and the catalyst of the amount weight of coats of 100g / L-support was acquired. The amount of hodium support was 13.33 g/cf (0.47 g/L) (catalyst T).

0060] Subsequently, after making a barium acetate solution adhere to the above-mentioned nature monolith support of catalyst component support cordierite, calcinated at 400 degrees C for 1 hour, 10 g/L was made to contain as BaO, and the down-stream catalyst U was acquired.

0061] The beta-zeolite powder 600 section of example of comparison preparation 5SiO₂/aluminum₂ O₃ =25, ZSM5 of SiO₂/aluminum₂ O₃ =50 The 200 sections and the USY100 section of SiO₂/aluminum₂ O₃ =25, With the 500 sections, 1500g of pure water was fed into the magnetic ball mill, the silica sol (SiO₂ as concentration 20%) was mixed and ground, and the slurry was obtained. This slurry liquid was made to adhere to Catalyst U, the slurry of the surplus in a cel was removed and dried in airstream, and it calcinated at 400 degrees C for 1 hour. The down-stream catalyst V of amount weight of coats 300 g/L-support was acquired.

0062] The beta-zeolite powder 600 section of example of comparison preparation 6SiO₂/aluminum₂ O₃ =25, ZSM5 of SiO₂/aluminum₂ O₃ =50 The 200 sections and the USY100 section of SiO₂/aluminum₂ O₃ =25, With the 500 sections, 1500g of pure water was fed into the magnetic ball mill, the silica sol (SiO₂ as concentration 20%) was mixed and ground, and the slurry was obtained. This slurry liquid was made to adhere to the catalyst U acquired in the example 4 of a comparison, the slurry of the surplus in a cel was removed and dried in airstream, and it calcinated at 400 degrees C for 1 hour. The down-stream catalyst W of amount weight of coats 200 g/L-support was acquired.

0063] The specification of each catalyst acquired in the above-mentioned examples 1-12 of preparation and the examples 1-6 of comparison preparation is shown in Tables 1 and 2.

0064]

Table 1]

調製例	組成	コート量 (g/L)	PM量 (g/L)	備考
1 触媒A	SiO ₂ /Al ₂ O ₃ =15, A型t45f [La _{0.65} Pr _{0.18} Al _{0.17}][Mn _{0.1} Cr _{0.1} Fe _{0.1} Al _{0.1} Co _{0.1}] _{0.9} Pd0.1%/La _{0.01} Zr _{0.32} Ce _{0.67} O _x SiO ₂ zol.	120.0 75.0 75.0 30.0	PM 0.075	触媒貯蔵・放出触媒
2 触媒E	SiO ₂ /Al ₂ O ₃ =24, B-t45f SiO ₂ /Al ₂ O ₃ =50, ZSM5 SiO ₂ /Al ₂ O ₃ =25, USY SiO ₂ zol. Pd11%/Ce3mol%, Zr3mol%, La2mol%, Al ₂ O ₃ Pd2.5%/La _{0.01} Zr _{0.32} Ce _{0.67} O _x Al ₂ O ₃ Rh2%/Zr3mol%, Al ₂ O ₃ La _{0.01} Ce _{0.22} Pr _{0.79} O _x Al ₂ O ₃ BaO	120.0 120.0 10.0 20.0 20.0 41.0 11.0 2.0 23.5 15.0 1.5 10.0	PM 5.18 Rh 0.47	内層: 炭化水素吸着材 中層: 貴金属成分層 外層: 貴金属成分層
3 触媒F	SiO ₂ /Al ₂ O ₃ =15, X型t45f [La _{0.55} Pr _{0.2} Ba _{0.2} Co _{0.05} Ni _{0.05}][Cr _{0.1} Mn _{0.3} Fe _{0.3} Al _{0.1} Ni _{0.1} Al _{0.05} Ti _{0.05}] _{0.9} Pd0.1%/La _{0.01} Zr _{0.32} Ce _{0.67} O _x SiO ₂ zol.	120.0 75.0 75.0 30.0	PM 0.075	触媒貯蔵・放出触媒
4 触媒G	SiO ₂ /Al ₂ O ₃ =15, A型t45f SiO ₂ /Al ₂ O ₃ =15, X型t45f [La _{0.55} Pr _{0.2} Ba _{0.2} Co _{0.05} Ni _{0.05}][Cr _{0.1} Mn _{0.3} Fe _{0.3} Al _{0.1} Ni _{0.1} Al _{0.05} Ti _{0.05}] _{0.9} Pd0.1%/La _{0.01} Zr _{0.32} Ce _{0.67} O _x SiO ₂ zol.	30.0 30.0 30.0 180.0 30.0	PM 0.18	触媒貯蔵・放出触媒
5 触媒H	SiO ₂ /Al ₂ O ₃ =15, A型t45f SiO ₂ /Al ₂ O ₃ =15, X型t45f [La _{0.65} Pr _{0.18} Al _{0.17}][Mn _{0.1} Cr _{0.1} Co _{0.1}] _{0.9} Pd0.1%/La _{0.01} Zr _{0.32} Ce _{0.67} O _x SiO ₂ zol.	15.0 15.0 30.0 240.0 30.0	PM 0.21	触媒貯蔵・放出触媒
6 触媒I	SiO ₂ /Al ₂ O ₃ =15, X型t45f [La _{0.65} Pr _{0.18} Al _{0.17}][Mn _{0.1} Cr _{0.1} Co _{0.1}] _{0.9} Pd0.1%/La _{0.01} Zr _{0.32} Ce _{0.67} O _x SiO ₂ zol.	15.0 15.0 240.0 30.0	PM 0.21	触媒貯蔵・放出触媒
7 触媒J	SiO ₂ /Al ₂ O ₃ =15, X型t45f [La _{0.95} Pr _{0.1}][Co _{0.1}] _{0.9} Pd0.1%/La _{0.01} Zr _{0.32} Ce _{0.67} O _x SiO ₂ zol.	15.0 15.0 240.0 30.0	PM 0.21	触媒貯蔵・放出触媒
8 触媒K	SiO ₂ /Al ₂ O ₃ =25, B-t45f SiO ₂ /Al ₂ O ₃ =50, ZSM5 SiO ₂ /Al ₂ O ₃ =25, USY SiO ₂ zol. Pd11%/Ce3mol%, Zr3mol%, La2mol%, Al ₂ O ₃ Pd2.5%/La _{0.01} Zr _{0.32} Ce _{0.67} O _x Al ₂ O ₃ Rh2%/Zr3mol%, Al ₂ O ₃ La _{0.01} Ce _{0.22} Pr _{0.79} O _x Al ₂ O ₃ BaO	150.0 30.0 10.0 20.0 41.0 11.0 2.0 23.5 15.0 1.5 10.0	PM 5.18 Rh 0.47	内層: 炭化水素吸着材 中層: 貴金属成分層 外層: 貴金属成分層
9 触媒L	SiO ₂ /Al ₂ O ₃ =50, B-t45f SiO ₂ zol. Pd11%/Ce3mol%, Zr3mol%, La2mol%, Al ₂ O ₃ Pd2.5%/La _{0.01} Zr _{0.32} Ce _{0.67} O _x Al ₂ O ₃ Rh2%/Zr3mol%, Al ₂ O ₃ La _{0.01} Ce _{0.22} Pr _{0.79} O _x Al ₂ O ₃ BaO	180.0 20.0 41.0 11.0 2.0 23.5 15.0 1.5 10.0	PM 5.18 Rh 0.47	内層: 炭化水素吸着材 中層: 貴金属成分層 外層: 貴金属成分層
10 触媒M	SiO ₂ /Al ₂ O ₃ =50, ZSM5 SiO ₂ /Al ₂ O ₃ =25, USY SiO ₂ zol. Pd11%/Ce3mol%, Zr3mol%, La2mol%, Al ₂ O ₃ Pd2.5%/La _{0.01} Zr _{0.32} Ce _{0.67} O _x Al ₂ O ₃ Rh2%/Zr3mol%, Al ₂ O ₃ La _{0.01} Ce _{0.22} Pr _{0.79} O _x Al ₂ O ₃ BaO	80.0 180.0 20.0 41.0 11.0 2.0 23.5 15.0 1.5 10.0	PM 5.18 Rh 0.47	内層: 炭化水素吸着材 中層: 貴金属成分層 外層: 貴金属成分層

[0065]

[Table 2]

実施例	組成	コート量 (g/L)	PM量 (g/L)	備考
11 触媒H	SiO ₂ /Al ₂ O ₃ =30, Ba _{0.5} wt%, Ca _{0.1} wt%, β - γ - Ce^{3+} 4%	180.0		内層: 炭化水素吸着材 中層: 貴金属成分層 表層: 貴金属成分層
	SiO ₂ sol.	20.0		
	Pd11%, Ce3mol%, Zr3mol%, La2mol%, Al ₂ O ₃	11.0	Pd 5.18	
	Pd2.5%, La _{0.01} Zr _{0.32} Ce _{0.67} O _x	11.0		
	Al ₂ O ₃	2.0		
	Rh2%/Zr3wt%, Al ₂ O ₃	21.5		
12 触媒O	La _{0.01} Ce _{0.22} Zr _{0.79} O _x	15.0	Rh 0.47	内層: 炭化水素吸着材 中層: 貴金属成分層 表層: 貴金属成分層
	Al ₂ O ₃	1.5		
	BaO	10.0		
	SiO ₂ /Al ₂ O ₃ =25, Pd _{0.1} wt%, Ag _{0.1} wt%, Pd _{0.1} wt%, β - γ - Ce^{3+} 4%	100.0		
	SiO ₂ /Al ₂ O ₃ =30, Pd _{0.1} wt%, Ag _{0.1} wt%, Ca _{0.1} wt%, ZSM5	20.0		
	SiO ₂ /Al ₂ O ₃ =25, Pd _{0.5} wt%, Ca _{0.1} wt%, USY	20.0		
比較 調製例	SiO ₂ sol.	20.0		内層: 炭化水素吸着材 中層: 貴金属成分層 表層: 貴金属成分層
	Pd11%, Ce3mol%, Zr3mol%, La2mol%, Al ₂ O ₃	11.0	Pd 5.18	
	Pd2.5%, La _{0.01} Zr _{0.32} Ce _{0.67} O _x	11.0		
	Al ₂ O ₃	2.0		
	Rh2%, Zr3wt%, Al ₂ O ₃	21.5		
	La _{0.01} Ce _{0.22} Zr _{0.79} O _x	15.0	Rh 0.47	
比較 調製例	Al ₂ O ₃	1.5		内層: 炭化水素吸着材と貴 金属成分層の配置を 逆転
	BaO	10.0		
	SiO ₂ /Al ₂ O ₃ =15, A型セライト			
	SiO ₂ sol.			
	[La _{0.05} Si _{0.38} Al _{0.1}][Mn _{0.4} Co _{0.4} Fe _{0.1} Al _{0.1}]O ₃			
	SiO ₂ sol.			
1 触媒P	Pd0.1%, La _{0.012} Zr _{0.32} Ce _{0.67} O _x			三元触媒 内層: 貴金属成分層 表層: 貴金属成分層
	SiO ₂ sol.			
	Pd11%, Ce3mol%, Zr3mol%, La2mol%, Al ₂ O ₃	11.0	Pd 5.18	
	Pd2.5%, La _{0.012} Zr _{0.32} Ce _{0.67} O _x	11.0		
	Al ₂ O ₃	2.0		
	Rh2%/Zr3wt%, Al ₂ O ₃	21.5		
2 触媒Q	La _{0.01} Ce _{0.22} Zr _{0.79} O _x	15.0	Rh 0.47	内層: 炭化水素吸着材と貴 金属成分層の配置を 逆転
	Al ₂ O ₃	1.5		
	BaO	10.0		
	SiO ₂ /Al ₂ O ₃ =25, Pd _{0.1} wt%, Ag _{0.1} wt%, Pd _{0.1} wt%, β - γ - Ce^{3+} 4%	120.0		
	SiO ₂ /Al ₂ O ₃ =30, Pd _{0.1} wt%, Ag _{0.1} wt%, Ca _{0.1} wt%, ZSM5	20.0		
	SiO ₂ /Al ₂ O ₃ =25, Pd _{0.5} wt%, Ca _{0.1} wt%, USY	20.0		
3 触媒R	SiO ₂ sol.	20.0		炭化水素吸着材 の触媒
	SiO ₂ /Al ₂ O ₃ =25, β - γ - Ce^{3+} 4%	120.0		
	SiO ₂ /Al ₂ O ₃ =30, ZSM5	20.0		
	SiO ₂ /Al ₂ O ₃ =25, USY	20.0		
	SiO ₂ sol.	20.0		
	SiO ₂ sol.	20.0		

[0066] examples 1-12 and the examples 1-7 of a comparison — the following durable conditions performed durability for each catalyst acquired in said examples 1-12 of preparation, and the examples 1-6 of comparison preparation.

[0067]

Durable conditions Engine displacement 3000 cc Fuel Unleaded gasoline Catalyst inlet gas temperature 500 degrees C Durable time amount 50 hours Inlet-port gas presentation CO 0.5**0.1% O₂ 0.5**0.1% HC About 1100 ppm NO 1300 ppm CO₂ 15% A/F fluctuation 2750 times (65 seconds/time, of periods)

Period: A/F=14.6 55 seconds Fuel cut 5 seconds Rich Spike 5 seconds (CO=2%)

[0068] Subsequently, it installed in the evaluation system which shows each catalyst after durability to the catalyst arrangement and drawing 1 which are shown in the following table 3, and the catalyst equipment for exhaust gas purification was obtained. The approach of purifying exhaust gas was performed on condition that the following using each equipment.

[0069]

Purification evaluation conditions Engine displacement Nissan Motor Co., Ltd. make V type 6-cylinder 3.3L Fuel Unleaded gasoline Evaluation mode LA4-CH (A-bag)

[0070] The evaluation result (emission value) measured on the above-mentioned purification conditions about each example and the example of a comparison is shown in Table 3.

[0071] However, a cold HC discharge arranges TWC to the catalyst arrangement 1, and measures base emission. TWC is arranged to the catalyst arrangement 1, it arranges each catalyst to arrangement 2 and 3, and the cold HC amount of adsorption is taken as difference with the above-mentioned base emission (for [of LA4Abag] 0 to 60 seconds). The amount of non-purified desorption HC considers difference with the base emission after 60 second as the non-purified desorption HC to the above-mentioned cold HC amount of adsorption. Moreover, [Equation 1]

〔コールドHC吸着量〕 - 〔未浄化脱離HC量〕

$$\text{脱離HC浄化率} = \frac{[\text{コールドHC吸着量}] - [\text{未浄化脱離HC量}]}{[\text{コールドHC吸着量}]} \times 100$$

The amount of desorption HC purification = it measured as an amount of cold HC amount-of-adsorption-non-purified desorption HC.
[0072]

Table 3]

	触媒配置			コールドHC 吸出量 (g/test)	コールドHC 吸着量 (g/test)	未浄化 脱離HC量 (g/test)	脱離HC 浄化率 (%)	脱離HC 浄化量 (g/test)
	1	2	3					
実施例 1	TWC	触媒A	触媒E	1.22	0.915	0.706	22.8	0.209
実施例 2	TWC	触媒F	触媒E	1.22	0.915	0.705	23.0	0.210
実施例 3	TWC	触媒G	触媒E	1.22	0.915	0.704	23.1	0.211
実施例 4	TWC	触媒H	触媒E	1.22	0.915	0.702	23.3	0.213
実施例 5	TWC	触媒I	触媒E	1.22	0.915	0.703	23.2	0.212
実施例 6	TWC	触媒J	触媒E	1.22	0.915	0.700	23.5	0.215
実施例 7	TWC	触媒A	触媒K	1.22	0.927	0.708	23.6	0.219
実施例 8	TWC	触媒F	触媒L	1.22	0.939	0.719	23.4	0.220
実施例 9	TWC	触媒G	触媒M	1.22	0.903	0.683	24.4	0.220
実施例 10	TWC	触媒H	触媒N	1.22	0.939	0.718	23.5	0.221
実施例 11	TWC	触媒I	触媒O	1.22	0.952	0.731	23.2	0.221
実施例 12	TWC	触媒J	触媒E	1.22	0.915	0.698	23.9	0.219
比較例 1	TWC	なし	触媒E	1.22	0.915	0.714	22.0	0.201
比較例 2	TWC	触媒P	触媒E	1.22	0.915	0.715	21.9	0.200
比較例 3	TWC	触媒Q	触媒E	1.22	0.915	0.715	21.9	0.200
比較例 4	TWC	触媒R	触媒E	1.22	0.915	0.713	22.0	0.202
比較例 5	TWC	触媒A	触媒U	1.22	0.915	0.810	0.55	0.005
比較例 6	TWC	触媒A	触媒V	1.22	0.915	0.759	17.0	0.156
比較例 7	TWC	触媒A	触媒W	1.22	0.915	0.915	0.000	0.000

[0073]

[Effect of the Invention] The exhaust gas purification approach according to claim 1 combines a catalyst with oxygen storage / emission ability, and the catalyst which has hydrocarbon adsorption and decontamination capacity. By supplying oxygen required for purification in case the catalyst which adsorbed the hydrocarbon in the low-temperature exhaust gas immediately after engine starting discharged by the internal combustion engine is desorbed from a hydrocarbon by the rise of catalyst bed temperature The purification engine performance of a hydrocarbon can be improved and the hydrocarbon discharged with un-purifying can be reduced sharply.

[0074] It adds to the above-mentioned effectiveness and the exhaust gas purification approach according to claim 2 is SiO₂ / aluminum 2O₃ as oxygen adsorption material. When a ratio uses 20 or less A mold and an X type zeolite Emission with separation and adsorption is easily controllable by the temperature change of a catalyst bed alternatively [oxygen], in case it is desorbed from a hydrocarbon by the rise of the catalyst bed temperature which adsorbed the hydrocarbon, oxygen required for purification can be supplied and the purification engine performance can be improved.

[0075] The exhaust gas purification approach according to claim 3 can control that the zeolite used as oxygen adsorption material is destroyed by heat in addition to the above-mentioned effectiveness, and this zeolite can aim at maintenance of the engine performance which separates, adsorbs and emits oxygen.

[0076] In addition to the above-mentioned effectiveness, the exhaust gas purification approach according to claim 4 can aim at improvement in the engine performance by which this catalyst dissociates and adsorbs oxygen, when thermal resistance contains an oxygen migratory high, high ingredient.

[0077] In addition to the above-mentioned effectiveness, the exhaust gas purification approach according to claim 5 can aim at improvement in the engine performance to which this catalyst emits oxygen.

[0078] In addition to the above-mentioned effectiveness, by combining various hydrocarbon adsorption material, the exhaust gas purification approach according to claim 6 adsorbs the hydrocarbon kind discharged at the time of the low temperature immediately after engine starting at high effectiveness, and can improve the decontamination capacity of the hydrocarbon moreover desorbed from a noble-metals component by contacting hydrocarbon adsorption material.

[0079] In addition to the above-mentioned effectiveness, the exhaust gas purification approach according to claim 7 adsorbs HC kind discharged at the time of the low temperature immediately after engine starting at high effectiveness, and moreover, since the structural change and performance degradation after durability are small, it can attain delay-ization of a desorption rate.

[0080] In addition to the above-mentioned effectiveness, the exhaust gas purification approach according to claim 8 can control the catalyst performance degradation resulting from reduction of a catalyst component.

[0081] In addition to the above-mentioned effectiveness, the exhaust gas purification approach according to claim 9 improves the purification engine performance further, and can control the catalyst performance degradation resulting from poisoning of a catalyst

component.

0082] In addition to the above-mentioned effectiveness, the exhaust gas purification approach according to claim 10 improves, carries out sintering control of the low-temperature activity of palladium further, and can improve endurance.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the schematic diagram showing an example of an evaluation system which enforces the exhaust gas purification
approach of this invention effectively.

[Translation done.]

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(71) 出願人 000003997

日産自動車株式会社

神奈川県横浜市神奈川区宝町2番地

(72) 発明者 山本 伸司

神奈川県横浜市神奈川区宝町2番地 日産
自動車株式会社内

(72) 発明者 高谷 真弘

神奈川県横浜市神奈川区宝町2番地 日産
自動車株式会社内

(74) 代理人 100059258

弁理士 杉村 暁秀 (外8名)

最終頁に続く

(54) 【発明の名称】 排気ガス浄化方法

(57) 【要約】

【課題】 低温排気ガスを浄化するにあたり、従来の触媒よりも耐久性が向上し、特に高温耐久後においても優れた低温活性と浄化性能、特に優れたHC浄化効率を示す排気ガス浄化方法を提供することにある。

【解決手段】 低温排気ガスを浄化するにあたり、排気ガス流れに対して上流側に、触媒層温度が室温から200℃の温度域で排気ガス中から酸素を選択的に分離・吸着する酸素貯蔵能を有し200℃～400℃の温度域で酸素放出能を有する酸素吸着材を含有する触媒を配置し、その下流側に室温から150℃の温度域で炭化水素吸着能を有し150℃の温度域で炭化水素脱離・浄化能を有する炭化水素吸着材と貴金属とを含有する触媒を配置し、前記上流側に配置した触媒の更に上流側に排気ガス流路切り換え可能なバルブを配置し、該下流側に配置した触媒が、その触媒層温度150℃～300℃の温度域で炭化水素を脱離・浄化する際に、該上流側の触媒から下流側の触媒に酸素が供給されるように上記触媒配置が設定され、前記バルブは上流側の触媒の触媒層中の温度に応じて調節される排気ガス浄化方法である。

【特許請求の範囲】

【請求項 1】 低温排気ガスを浄化するにあたり、排気ガス流れに対して上流側に、触媒層温度が室温から 200℃の温度域で排気ガス中から酸素を選択的に分離・吸着する酸素貯蔵能を有し 200℃～400℃の温度域で酸素放出能を有する酸素吸着材を含有する触媒を配置し、その下流側に室温から 150℃の温度域で炭化水素吸着能を有し 150℃の温度域で炭化水素脱離・浄化能を有する炭化水素吸着材と貴金属とを含有する触媒を配置し、前記上流側に配置した触媒の更に上流側に排気ガス流路切り換え可能なバルブを配置し、該下流側に配置した触媒が、その触媒層温度 150℃～300℃の温度域で炭化水素を脱離・浄化する際に、該上流側の触媒から下流側の触媒に酸素が供給されるように上記触媒配置が設定され、前記バルブは上流側の触媒の触媒層中の温度に応じて調節されることを特徴とする排気ガス浄化方法。

【請求項 2】 上流側に配置した触媒は、酸素吸着材として、 $\text{SiO}_2/\text{Al}_2\text{O}_3$ 比が 20 以下の A 型および X ゼオライトを含有することを特徴とする請求項 1 に記載の排気ガス浄化方法。

【請求項 3】 上流側に配置した触媒の触媒層中の温度が 400℃に到達した際に、該触媒の上流側に設置したバルブを作動させ、排気ガス流路を切り替えて 400℃以上の温度を排気ガスが当該上流側に配置した触媒に流れ込むことを防止することを特徴とする請求項 1 又は 2 記載の排気ガス浄化方法。

【請求項 4】 上流側に配置した触媒は、次の組成式：
[A] [B] O_y

(式中、A は La、Sr、Ba、Pb、Nd 及び Ce からなる群より選ばれた一種以上の元素、B は Al、Ti、Cr、Mn、Co、Fe 及び Ni からなる群より選ばれた一種以上の元素、O は酸素を示し、y は各元素の原子価を満足するのに必要な酸素原子数を示す) で表されるペロブスカイト型構造の複合酸化物を含有することを特徴とする請求項 1～3 いずれかの項記載の排気ガス浄化方法。

【請求項 5】 上流側に配置した触媒は、白金及び／又はパラジウムを担持したセリウム酸化物を含有することを特徴とする請求項 1～4 記載の排気ガス浄化方法。

【請求項 6】 下流側に配置した触媒は、炭化水素吸着材として ZSM5、USY 及び β-ゼオライトからなる群より選ばれた一種以上のゼオライトと、貴金属として白金、パラジウム及びロジウムからなる群より選ばれた一種以上の金属と、活性アルミナと、セリア酸化物と、ジルコニウム酸化物と、バリウム化合物とを含有することを特徴とする請求項 1～5 記載の排気ガス浄化方法。

【請求項 7】 炭化水素吸着材は、白金、パラジウム、リン、ホウ素、マグネシウム及びカルシウムからなる群より選ばれた一種以上の元素を含有することを特徴とす

る請求項 6 記載の排気ガス浄化方法。

【請求項 8】 炭化水素吸着材層の上部に、パラジウムと、ジルコニウム、ネオジウム及びランタンからなる群より選ばれた一種以上の元素を金属換算で 1～40 モル % 及びセリウムを 60～98 モル % 含むセリウム酸化物とを含有する触媒成分層が配置されることを特徴とする請求項 6 又は 7 記載の排気ガス浄化方法。

【請求項 9】 炭化水素吸着材層の上部に配置したパラジウムを含有する触媒成分層の上部に、更に、白金、ロジウム、セリウム、ネオジウム及びランタンからなる群より選ばれた一種以上の元素を金属換算で 1～30 モル % ジルコニウムを 70～98 % 含むジルコニウム酸化物と、活性アルミナとを含有する触媒成分層が配置されることを特徴とする請求項 8 記載の排気ガス浄化方法。

【請求項 10】 炭化水素吸着材層の上部に、アルカリ金属及びアルカリ土類金属からなる群より選ばれた少なくとも一種が含有される三元触媒が配置されることを特徴とする請求項 8 又は 9 記載の排気ガス浄化方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、排気ガス浄化方法に関し、特に自動車等の内燃機関からエンジン始動直後の低温時に排出される排気ガス中の炭化水素（以下、「HC」と称す）、一酸化炭素（以下「CO」と称す）及び窒化酸化物（以下、「NO_x」と称す）のうち、特に、HC を効率良く浄化することができる排気ガス浄化方法に関する。

【0002】

【従来の技術】従来より、排気ガス浄化用触媒は高温下での耐久性が十分でなく、触媒が劣化し浄化能が著しく低下するため、エンジン始動直後の低温時に排出される排気ガス中の炭化水素（以下、「コールドHC」と称す）の低減を目的に、HC 吸着材を用いて一時的に貯蔵し、三元触媒が活性化した後、脱離させて該三元触媒で浄化する方法が検討されている。

【0003】かかる HC 吸着材を用いた排気ガス浄化用触媒としては、例えば、特開平 6-74019 号公報、特開平 7-144119 号公報、特開平 6-142457 号公報、特開平 5-59942 号公報又は特開平 7-102957 号公報等に記載されているものがある。

【0004】特開平 6-74019 号公報には、排気流路にバイパス流路を設け、エンジン始動直後のコールド時に排出される HC をバイパス流路に配置した HC 吸着材に一旦吸着させ、その後排気流路を切り換えて、下流の三元触媒が活性化した後、排気ガスの一部を HC 吸着触媒に通じ、脱離した HC を徐々に後段の三元触媒で浄化するシステムが提案されている。

【0005】特開平 7-144119 号公報には、エンジン始動直後のコールド時に前段の三元触媒に熱を奪われて中段の HC 吸着材の吸着効率を向上させ、前段の三

元触媒活性化後は、タンデム配置した中段のHC吸着材を介して後段の三元触媒に反応熱を伝熱し易くし、後段の三元触媒での浄化を促進するシステムが提案されている。

【0006】特開平6-142457号公報には、低温域で吸着したHCが脱離する際に、脱離HCを含む排気ガスを熱交換器で予熱し、三元触媒での浄化を促進するコールドHC吸着除去システムが提案されている。

【0007】特開平5-59942号公報には、触媒配置とバルブによる排気ガスの流路を切り換えることによ
10 って、HC吸着材の昇温を緩慢にし、コールドHCの吸着効率を向上するシステムが提案されている。

【0008】また、特開平7-102957号公報には、後段の酸化・三元触媒の浄化性能を向上するため、前段の三元触媒と中段のHC吸着材との間に空気を供給し、後段の酸化・三元触媒の活性化を促進するシステムが提案されている。

【0009】

【発明が解決しようとする課題】しかし、前記公報中に記載されたHC吸着材を用いた従来のシステムでは、HC
20 吸着材の耐久性が不十分なため、耐久後にはHC吸着効率が低下し、しかも、後段の三元触媒が活性化する前にHCが脱離してしまいエミッションを悪化させてしまう。

【0010】そこで、HC吸着材の吸着効率の向上や脱離遅延化を図るため、高温ガスのバイパス法や三元触媒暖気のための熱交換器が使用されているが、システム構成が複雑化する一方で、十分な効果が得られず、しか
30 も、コストが著しく上昇するため、耐久性と吸着効率の高いHC吸着材が望まれている。

【0011】特に、HC吸着材から脱離するHCの浄化を目的とした三元触媒は、初期から耐久後まで高い浄化性能を維持するために貴金属を多量に使用したり、早期活性化と脱離HCの浄化促進を図るために空気を導入してりしている。このため、使用する貴金属量が少なくとも高い浄化性能が得られる触媒が望まれているが、貴金属を低減した場合には、耐久性が不十分となり、耐久後は低温域での触媒活性や浄化性能が悪化するという問題があった。

【0012】従って、本発明の目的は、低温排気ガスを
40 浄化するにあたり、従来の触媒よりも耐久性が向上し、特に高温耐久後においても優れた低温活性と浄化性能、特に優れたHC浄化効率を示す排気ガス浄化方法を提供することにある。

【0013】

【課題を解決するための手段】本発明者らは、上記課題を解決するために研究した結果、内燃機関から排出されるエンジン始動直後の低温排気ガスの浄化において、排気ガスの上流側に酸素貯蔵・放出能を有する触媒を、その下流側に炭化水素吸着・浄化能を有する触媒を配置
50

し、下流側の触媒が炭化水素を脱離・浄化する際に、上流側の触媒から下流側の触媒に酸素を供給することによって、吸着したコールドHCが脱離する際のHC浄化効率が著しく向上・維持されることを見出し、本発明に到達した。

【0014】請求項1記載の排気ガス浄化方法は、低温排気ガスを浄化するにあたり、排気ガス流れに対して上流側に、触媒層温度が室温から200℃の温度域で排気ガス中から酸素を選択的に分離・吸着する酸素貯蔵能を有し200℃～400℃の温度域で酸素放出能を有する酸素吸着材を含有する触媒を配置し、その下流側に室温から150℃の温度域で炭化水素吸着能を有し150℃の温度域で炭化水素脱離・浄化能を有する炭化水素吸着材と貴金属とを含有する触媒を配置し、前記上流側に配置した触媒の更に上流側に排気ガス流路切り換え可能なバルブを配置し、該下流側に配置した触媒が、その触媒層温度150℃～300℃の温度域で炭化水素を脱離・浄化する際に、該上流側の触媒から下流側の触媒に酸素が供給されるように上記触媒配置が設定され、前記バルブは上流側の触媒の触媒層中の温度に応じて調節されることを特徴とする。

【0015】請求項2記載の排気ガス浄化方法は、請求項1記載の排気ガス浄化方法において、上流側に配置した触媒が、酸素吸着材として、 $\text{SiO}_2/\text{Al}_2\text{O}_3$ 比が20以下のA型およびXゼオライトを含有することを特徴とする。

【0016】請求項3記載の排気ガス浄化方法は、請求項1又は2記載の排気ガス浄化方法において、上流側に配置した触媒の触媒層中の温度が400℃に到達した際に、該触媒の上流側に設置したバルブを作動させ、排気ガス流路を切り替えて400℃以上の温度を排気ガスが当該上流側に配置した触媒に流れ込むことを防止することを特徴とする。

【0017】請求項4記載の排気ガス浄化方法は、請求項1～3いずれかの項記載の排気ガス浄化方法において、上流側に配置した触媒が、次の組成式：[A]
[B] O_y (式中、AはLa、Sr、Ba、Pb、Nd及びCeからなる群より選ばれた一種以上の元素、Bは、Al、Ti、Cr、Mn、Co、Fe及びNiからなる群より選ばれた一種以上の元素、Oは酸素を示し、yは各元素の原子価を満足するのに必要な酸素原子数を示す) で表されるペロブスカイト型構造の複合酸化物を含有することを特徴とする。

【0018】請求項5記載の排気ガス浄化方法は、請求項1～4いずれかの項記載の排気ガス浄化方法において、上流側に配置した触媒が、白金及び／又はパラジウムを担持したセリウム酸化物を含有することを特徴とする。

【0019】請求項6記載の排気ガス浄化方法は、請求項1～5いずれかの項記載の排気ガス浄化方法におい

て、下流側に配置した触媒が、炭化水素吸着材として ZSM5、USY 及び β -ゼオライトからなる群より選ばれた一種以上のゼオライトと、貴金属として白金、パラジウム及びロジウムからなる群より選ばれた一種以上の金属と、活性アルミナと、セリア酸化物と、ジルコニウム酸化物と、バリウム化合物とを含有することを特徴とする。

【0020】請求項7記載の排気ガス浄化方法は、請求項6記載の排気ガス浄化方法において、炭化水素吸着材が、白金、パラジウム、リン、ホウ素、マグネシウム及びカルシウムからなる群より選ばれた一種以上の元素を含有することを特徴とする。

【0021】請求項8記載の排気ガス浄化方法は、請求項7記載の排気ガス浄化方法において、炭化水素吸着材層の上部に、パラジウムと、ジルコニウム、ネオジウム及びランタンからなる群より選ばれた一種以上の元素を金属換算で1~40モル%及びセリウムを60~98モル%含むセリウム酸化物とを含有する触媒成分層が配置されることを特徴とする。

【0022】請求項9記載の排気ガス浄化方法は、請求項8記載の排気ガス浄化方法において、炭化水素吸着材層の上部に配置したパラジウムを含有する触媒成分層の上部に、更に、白金、ロジウム、セリウム、ネオジウム及びランタンからなる群より選ばれた一種を金属換算で1~30モル%ジルコニウムを70~98%含むジルコニウム酸化物と、活性アルミナとを含有する触媒成分層が配置されることを特徴とする請求項8記載の排気ガス浄化方法。

【0023】請求項10記載の排気ガス浄化方法は、請求項8又は9記載の排気ガス浄化方法において、炭化水素吸着材層の上部にアルカリ金属及びアルカリ土類金属からなる群より選ばれた少なくとも一種が含有されている三元触媒が配置されることを特徴とする。

【0024】

【発明の実施の形態】本発明の排気ガス浄化方法としては、内燃機関から排出されるエンジン始動直後の低温排気ガスを浄化するにあたり、排気ガス流れに対して上流側に、触媒層温度が室温から200℃の温度域で排気ガス中から酸素を選択的に分離・吸着する酸素貯蔵能を有し200℃~400℃の温度域で酸素放出能を有する酸素吸着材を含有する触媒を配置し、その下流側に室温から150℃の温度域で炭化水素吸着能を有し150℃の温度域で炭化水素脱離・浄化能を有する炭化水素吸着材と貴金属とを含有する触媒を配置し、前記上流側に配置した触媒の更に上流側に排気ガス流路切り換え可能なバルブを配置し、該下流側に配置した触媒が、その触媒層温度150℃~300℃の温度域で炭化水素を脱離・浄化する際に、該上流側の触媒から下流側の触媒に酸素が供給されるように上記触媒配置が設定され、前記バルブは上流側の触媒の触媒層中の温度に応じて調節される構

成とすることによって、該下流側の触媒の脱離炭化水素浄化効率を向上することができる。

【0025】上流側に配置した触媒が含有する酸素貯蔵・供給能を有する酸素吸着材材料は、低温排気ガス中から酸素を選択的に分離・吸着できる $\text{SiO}_2/\text{Al}_2\text{O}_3$ 比が20以下のA型及びX型ゼオライトが有効である。該ゼオライトを含有させた触媒は、触媒層温度が室温から200℃の温度域で排気ガス中の酸素を選択的に分離・貯蔵し、200℃から400℃の温度域で酸素を放出でき、下流側の触媒が低温排気ガスから吸着した炭化水素を脱離・浄化する際に酸素を効率的に供給でき、貴金属のHC浄化効率を向上させることができる。その量は、触媒1Lあたり10g~300gが性能向上の点から好ましい。

【0026】また、該上流側の触媒層中の温度（当該触媒層中に温度検出器を設置して温度を検出）が400℃に到達した際に、該触媒の上流側に設置したバルブを作動させて排気ガス流路を切り替えるが、これは400℃以上の温度の排気ガスが酸素吸着材に流れ込むことを防止して、該ゼオライトの熱による構造破壊を防止するためである。

【0027】また、該上流側に配置した触媒が、触媒層温度の上昇により200℃以上の温度域で酸素を放出するため、耐熱性に優れた材料として、次の組成式：

【A】 $[\text{B}]_y\text{O}_x$

（Aは、La、Sr、Ba、Pb、Nd、Ceからなる群より選ばれた一種以上の元素、Bは、Al、Ti、Cr、Mn、Co、Fe、Niからなる群より選ばれた一種以上の元素、Oは酸素を示し、yは各元素の原子価を満足するのに必要な酸素原子数を示す）で表される酸素移動性の高いペロブスカイト型構造の複合酸化物を含有することができる。このことによって、該上流側に配置した酸素吸着材たるゼオライトの性能低下を補うことができ、該下流側に配置した触媒の脱離炭化水素の浄化効率を更に向上できる。

【0028】更に、該上流側に配置した触媒が、触媒層温度の上昇により200℃以上の温度域で酸素を放出する作用を促進するため、白金及び/又はパラジウムを担持したセリウム酸化物を含有させることができる。該触媒に、白金及び/又はパラジウム担持セリウム酸化物を含有させることによって、上流側に配置した触媒の耐久性が向上し、該下流側に配置した触媒の脱離炭化水素の浄化効率を長期間に渡って向上できる。

【0029】上流側に配置した触媒が含有する酸素貯蔵・供給能を有する材料の合計使用量としては、上記、 $\text{SiO}_2/\text{Al}_2\text{O}_3$ 比が20以下のA型及びX型ゼオライトと、ペロブスカイト型構造の複合酸化物と、白金及び/又はパラジウムを担持したセリウム酸化物とを組合せて、上流触媒1Lあたり10g~300gが好ましい。酸素貯蔵・供給能を有する材料の使用量が10g未

満では吸着性能が十分に発現せず、逆に 300 g を越えても吸着性能は飽和し、経済的にも有効でない。

【0030】また、下流側に配置される、低温域で排出される炭化水素を吸着する材料としては、 $\text{SiO}_2/\text{Al}_2\text{O}_3$ 比が 20 以上の ZSM5、USY 及び β -ゼオライトからなる群より選ばれた一種以上を用いることによって、低温域で排出される種々の炭化水素を効率良く吸着することができる。炭化水素吸着材の使用量は、触媒 1 L あたり 10 g ~ 300 g が好ましい。炭化水素吸着材の使用量が 10 g 未満では吸着性能が十分に発現せず、逆に 300 g を越えても吸着性能は飽和し、経済的にも有効でない。更に、該炭化水素吸着材から脱離する炭化水素を浄化するため、貴金属として白金、パラジウム及びロジウムからなる群より選ばれた一種以上の元素と、活性アルミナと、セリア酸化物と、ジルコニウム酸化物と、バリウム化合物とを含有することによって、触媒層温度の上昇に伴って脱離する炭化水素を効率良く浄化することができる。その量は触媒 1 L あたり、貴金属は 1 g ~ 30 g、活性アルミナは 10 g ~ 300 g、セリア酸化物は 5 g ~ 100 g、ジルコニウム酸化物は 5 g ~ 100 g、バリウム化合物は 1 g ~ 50 g であることが脱離 HC を効率良く浄化する点から好ましい。

【0031】更に、炭化水素吸着材の高温下における構造安定性（耐熱性）と、コールド HC の吸着能や温度上昇時の HC 脱離抑制性能を向上するため、白金、パラジウム、リン、ホウ素、マグネシウム及びカルシウムからなる群より選ばれた一種以上の元素を含有することができる。かかる元素の含有量は、HC 吸着材に対して、0.1 重量% から 10 重量% である。0.1 重量% 未満だと十分な改良効果が得られず、逆に、10 重量% より多く使用すると、ゼオライトの細孔が閉塞し HC 吸着能が低下する。

【0032】更に、炭化水素吸着材で吸着した HC が脱離する際の浄化効率を向上するため、該炭化水素吸着材層の上部に、パラジウムと、ジルコニウム、ネオジウム及びランタンからなる群より選ばれた一種以上の元素を金属換算で 1 ~ 40 モル% セリウムを 60 ~ 98 モル% 含むセリウム酸化物とを含有する触媒成分層を配置することができる。特に、パラジウムの浄化性能と耐久性を向上させるため、パラジウム含有触媒成分層中に、ジルコニウム、ネオジウム及びランタンからなる群より選ばれた一種以上の元素を金属換算で 1 ~ 40 モル% セリウムを 60 ~ 98 モル% 含むセリウム酸化物を含有させることによって、酸素吸蔵能の高いセリウム酸化物が、リッチ雰囲気及びストイキ近傍で格子酸素や吸着酸素を放出し易くなるため、パラジウムの酸化状態を排気ガスの浄化に適したものとし、パラジウムの触媒能の低下を抑制できる。かかるパラジウムの使用量は、触媒 1 L あたり 1 g ~ 30 g であることが浄化性能の点から好ましい。かかるセリウム酸化物の使用量は、触媒 1 L あたり

5 ~ 100 g である。5 g 未満だと十分な貴金属の分散性が得られず、100 g より多く使用しても改良効果は飽和し有効でない。

【0033】更に、パラジウムの耐被毒性や浄化性能を向上するため、パラジウムを含有する触媒成分層の上部に、白金、ロジウム、セリウム、ネオジウム及びランタンからなる群より選ばれた一種以上の元素を金属換算で 1 ~ 30 モル% ジルコニウムを 70 ~ 98 モル% 含むジルコニウム酸化物と活性アルミナとを含有する触媒成分層を配置することができる。前記白金やロジウムが担持される基材としては、白金やロジウムの耐久性を向上させるため、ジルコニウム酸化物が適切である。特に、酸素吸蔵能の高いセリウム含有ジルコニウム酸化物が、リッチ雰囲気及びストイキ近傍で格子酸素や吸着酸素を放出し易くなるため、白金やロジウムの酸化状態を排気ガスの浄化に適したものとし、白金やロジウムの触媒能の低下を抑制できる。

【0034】かかるジルコニウム酸化物のセリウム含有量は 0.01 モル% から 30 モル% である。セリウム含有量が 0.01 モル% 未満では ZrO_2 のみの場合と変わらず、上記した元素の ZrO_2 のセリウムの酸素吸蔵能による改良効果が現れず、また、セリウム含有量が 30 モル% を越えるとこの効果が飽和もしくは逆に BET 比表面積や熱安定性が低下する。ジルコニウム酸化物の使用量は、触媒 1 L あたり 5 ~ 100 g である。5 g 未満だと十分な貴金属の分散性が得られず、100 g より多く使用しても改良効果は飽和し有効でない。

【0035】また、パラジウムの低温活性を向上するため、アルカリ金属及び／又はアルカリ土類金属を含有する三元触媒を配置することができる。これらの金属には、例えばカリウム、カルシウム、ストロンチウム、バリウム、ナトリウム、マグネシウム、イットリウムやランタン等がある。かかる元素の含有量は触媒 1 L 中 1 ~ 40 g である。1 g 未満では、HC 類の貴金属に対する吸着被毒の緩和やパラジウムのシントリングを抑制できず、逆に、40 g を越えても有為な増量効果が得られず逆に性能を低下させる。

【0036】

【実施例】本発明を次の調製例、実施例及び比較例により説明する。特に表示がない限り、部は重量部示す。

【0037】調製例 1

$\text{SiO}_2/\text{Al}_2\text{O}_3 = 15$ の A 型ゼオライト粉末を 400 部、組成式： $[\text{La}_{0.5}\text{Sr}_{0.5}\text{Ba}_{0.1}][\text{Mn}_{0.4}\text{Co}_{0.4}\text{Fe}_{0.1}\text{Al}_{0.1}]\text{O}_7$ のペロブスカイト型複合酸化物粉末を 250 部、パラジウム担持濃度 0.1 % のパラジウム担持セリウム酸化物 ($\text{La}_{0.01}\text{Zr}_{0.99}\text{Ce}_{0.01}\text{O}_3$) 粉末を 250 部と、シリカゾル (SiO_2 濃度として 20 %) を 500 部と、純水 2000 g とを磁性ボールミルに投入し、混合・粉砕してスラリーを得た。このスラリー液をコージェライト質モノリス

担体 (1.0 L、400セル) に付着させ、空気流にてセル内の余剰のスラリーを除去・乾燥し、400℃で1時間焼成した。この作業を2度行い、コート量重量300 g/Lー担体の上流触媒Aを得た。パラジウム担持量は2.12 g/cf (0.075 g/L) であった。

【0038】調製例2

SiO₂/Al₂O₃=25のβ-ゼオライト粉末を600部、SiO₂/Al₂O₃=50のZSM5を200部、SiO₂/Al₂O₃=25のUSYを100部と、シリカゾル (SiO₂濃度として20%) を500部と、純水1500 gとを磁性ボールミルに投入し、混合・粉砕してスラリーを得た。このスラリー液をコージェライト質モノリス担体 (1.0 L、400セル) に付着させ、空気流にてセル内の余剰のスラリーを除去・乾燥し、400℃で1時間焼成した。この作業を2度行い、コート量重量200 g/Lー担体の上流触媒を得た (触媒B)。

【0039】セリウム3モル% (CeO₂に換算して8.7重量%)、ジルコニウム3モル% (ZrO₂に換算して6.3重量%)とランタン2モル% (La₂O₃に換算して5.5重量%)を含有するアルミナ粉末 (粉末A) に硝酸パラジウム水溶液を含浸し、150℃で12時間乾燥した後、400℃で1時間焼成して、Pd担持アルミナ粉末 (粉末B) を得た。この粉末BのPd濃度は11重量%であった。

【0040】ランタン1モル% (La₂O₃に換算して2重量%)とジルコニウム32モル% (ZrO₂に換算して25重量%)を含むセリウム酸化物粉末 (粉末C) に硝酸パラジウム水溶液を含浸し、150℃で12時間乾燥した後、400℃で1時間焼成して、Pd担持セリウム酸化物 (La_{0.01}Zr_{0.32}Ce_{0.67}O_x) 粉末 (粉末D) を得た。この粉末DのPd濃度は2.5重量%であった。

【0041】上記粉末B880 g、粉末D280 g、活性アルミナ40 g及び硝酸水溶液1500 gを磁性ボールミルに投入し、混合・粉砕してスラリーを得た。このスラリー液を触媒Bに付着させ、空気流にてセル内の余剰のスラリーを除去・乾燥し、400℃で1時間焼成した。この作業を2度行い、コート量重量260 g/Lー担体の触媒を得た。パラジウム担持量は146.67 g/cf (5.18 g/L) であった (触媒C)。

【0042】次いで、Zr3重量%を担持した活性アルミナ物粉末 (粉末E) に硝酸ロジウム水溶液を含浸し、150℃で12時間乾燥した後、400℃で1時間焼成して、Rh担持Zr3重量%-Al₂O₃粉末 (粉末F) を得た。この粉末FのRh濃度は2.0重量%であった。

【0043】上記粉末Eを470部と、La1モル%、Ce20モル%、Zr79モル%のジルコニウム酸化物粉末 (粉末F) を300部と、活性アルミナ30部と、

硝酸水溶液1500 gを磁性ボールミルに投入し、混合・粉砕してスラリーを得た。このスラリー液を触媒Cに付着させ、空気流にてセル内の余剰のスラリーを除去・乾燥し、400℃で1時間焼成した。この作業を2度行い、コート量重量300 g/Lー担体の触媒を得た。ロジウム担持量は13.33 g/cf (0.47 g/L) であった (触媒D)。

【0044】次いで、上記触媒成分担持コージェライト質モノリス担体に酢酸バリウム溶液を付着させた後、400℃で1時間焼成し、BaOとして10 g/Lを含有させて下流触媒をE得た。

【0045】調製例3

SiO₂/Al₂O₃=15のA型ゼオライト粉末400部に代わり、SiO₂/Al₂O₃=15のX型ゼオライト粉末を400部とし、組成式: [La_{0.5}Sr_{0.5}Ba_{0.1}] [Mn_{0.4}Co_{0.4}Fe_{0.1}Al_{0.1}] O_yのペロブスカイト型複合酸化物粉末250部に代わり、組成式 [La_{0.5}Sr_{0.5}Ba_{0.2}Ce_{0.05}Nd_{0.05}] [Cr_{0.1}Mn_{0.3}Fe_{0.1}Ni_{0.1}Al_{0.05}Ti_{0.05}] O_yのペロブスカイト型複合酸化物粉末を250部とし、白金担持濃度0.1重量%の白金担持セリウム酸化物 (La_{0.01}Zr_{0.32}Ce_{0.67}O_x) 粉末の量を250部として用いた以外は、実施例1に準じて上流触媒Fを得た。

【0046】調製例4

SiO₂/Al₂O₃=15のA型ゼオライト粉末400部に代わり、Al₂O₃/Al₂O₃=15のA型ゼオライト粉末を100部及びSiO₂/Al₂O₃=15のX型ゼオライト粉末を100部とし、組成式: [La_{0.5}Sr_{0.5}Ba_{0.1}] [Mn_{0.4}Co_{0.4}Fe_{0.1}Al_{0.1}] O_yのペロブスカイト型複合酸化物粉末250部に代わり、組成式 [La_{0.5}Sr_{0.5}Ba_{0.2}Ce_{0.05}Nd_{0.05}] [Cr_{0.1}Mn_{0.3}Fe_{0.1}Ni_{0.1}Al_{0.05}Ti_{0.05}] O_yのペロブスカイト型複合酸化物粉末を100部とし、パラジウム担持濃度0.1重量%のパラジウム担持セリウム酸化物 (La_{0.01}Zr_{0.32}Ce_{0.67}O_x) 粉末の量を600部として用いた以外は、実施例1に準じ、上流触媒Gを得た。

【0047】調製例5

SiO₂/Al₂O₃=15のA型ゼオライト粉末400部に代わり、SiO₂/Al₂O₃=15のA型ゼオライト粉末を50部及びSiO₂/Al₂O₃=15のX型ゼオライト粉末を50部とし、組成式: [La_{0.5}Sr_{0.5}Ba_{0.1}] [Mn_{0.4}Co_{0.4}Fe_{0.1}Al_{0.1}] O_yのペロブスカイト型複合酸化物粉末250部に代わり、組成式 [La_{0.5}Sr_{0.5}Ba_{0.1}] [Mn_{0.1}Co_{0.9}] O_yのペロブスカイト型複合酸化物粉末を100部とし、パラジウム担持濃度0.1重量%のパラジウム担持セリウム酸化物 (La_{0.01}Zr_{0.32}Ce_{0.67}O_x) 粉末の量を700部として用いた以外は、実

施例1に準じ、上流触媒Hを得た。

【0048】調製例6

$\text{SiO}_2/\text{Al}_2\text{O}_3=15$ のA型ゼオライト粉末400部に代わり、 $\text{SiO}_2/\text{Al}_2\text{O}_3=15$ のA型ゼオライト粉末を50部とし、組成式： $[\text{La}_{0.6}\text{Sr}_{0.3}\text{Ba}_{0.1}][\text{Mn}_{0.4}\text{Co}_{0.4}\text{Fe}_{0.1}\text{Al}_{0.1}]\text{O}_x$ のペロブスカイト型複合酸化物粉末250部に代わり、組成式 $[\text{La}_{0.9}\text{Sr}_{0.1}\text{Ba}_{0.1}][\text{Mn}_{0.1}\text{Co}_{0.9}]\text{O}_x$ のペロブスカイト型複合酸化物粉末50部とし、パラジウム担持濃度0.1重量%のパラジウム担持セリウム酸化物($\text{La}_{0.01}\text{Zr}_{0.99}\text{Ce}_{0.99}\text{O}_x$)粉末の量を900部として用いた以外は、実施例1に準じ、上流触媒Hを得た。

【0049】調製例7

$\text{SiO}_2/\text{Al}_2\text{O}_3=15$ のA型ゼオライト粉末400部に代わり、 $\text{SiO}_2/\text{Al}_2\text{O}_3=15$ のX型ゼオライト粉末を50部とし、組成式： $[\text{La}_{0.6}\text{Sr}_{0.3}\text{Ba}_{0.1}][\text{Mn}_{0.4}\text{Co}_{0.4}\text{Fe}_{0.1}\text{Al}_{0.1}]\text{O}_x$ のペロブスカイト型複合酸化物粉末250部に代わり、組成式 $[\text{La}_{0.9}\text{Sr}_{0.1}]\text{O}_x$ のペロブスカイト型複合酸化物粉末を50部とし、パラジウム担持濃度0.1重量%のパラジウム担持セリウム酸化物($\text{La}_{0.01}\text{Zr}_{0.99}\text{Ce}_{0.99}\text{O}_x$)粉末の量を800部として用いた以外は、実施例1に準じ、上流触媒Jを得た。

【0050】調製例8

$\text{SiO}_2/\text{Al}_2\text{O}_3=25$ のβ-ゼオライト粉末600部、 $\text{SiO}_2/\text{Al}_2\text{O}_3=50$ のZSM5 200部、 $\text{SiO}_2/\text{Al}_2\text{O}_3=25$ のUSY100部に代わり、 $\text{SiO}_2/\text{Al}_2\text{O}_3=25$ のβ-ゼオライト粉末の量を800部、 $\text{SiO}_2/\text{Al}_2\text{O}_3=50$ のZSM5の量を50部、 $\text{SiO}_2/\text{Al}_2\text{O}_3=25$ のUSYの量を50部として用いた以外は、実施例2に準じ、下流触媒Kを得た。

【0051】調製例9

$\text{SiO}_2/\text{Al}_2\text{O}_3=25$ のβ-ゼオライト粉末600部に代わり、 $\text{SiO}_2/\text{Al}_2\text{O}_3=25$ のβ-ゼオライト粉末の量を900部として用い、更に、 $\text{SiO}_2/\text{Al}_2\text{O}_3=50$ のZSM5及び $\text{SiO}_2/\text{Al}_2\text{O}_3=25$ のUSYを用いない以外は、実施例2に準じ、下流触媒Lを得た。

【0052】調製例10

$\text{SiO}_2/\text{Al}_2\text{O}_3=50$ のZSM5 200部、 $\text{SiO}_2/\text{Al}_2\text{O}_3=25$ のUSY100部に代わり、 $\text{SiO}_2/\text{Al}_2\text{O}_3=50$ のZSM5を400部、 $\text{SiO}_2/\text{Al}_2\text{O}_3=25$ のUSYの量を500部として用い、更に $\text{SiO}_2/\text{Al}_2\text{O}_3=25$ のβ-ゼオライト粉末を用いない以外は、実施例2に準じ、下流触媒Mを得た。

【0053】調製例11

$\text{SiO}_2/\text{Al}_2\text{O}_3=50$ のβ-ゼオライト粉末90

0部に代わり、ホウ素0.5重量%、カルシウム0.1重量%を含む $\text{SiO}_2/\text{Al}_2\text{O}_3=50$ のβ-ゼオライト900部を用いた以外は、実施例9に準じ、下流触媒Nを得た。

【0054】調製例12

$\text{SiO}_2/\text{Al}_2\text{O}_3=25$ のβ-ゼオライト粉末600部、 $\text{SiO}_2/\text{Al}_2\text{O}_3=50$ のZSM5 200部、 $\text{SiO}_2/\text{Al}_2\text{O}_3=25$ のUSY100部に代わり、リン0.1重量%、マグネシウム0.1重量%、パラジウム0.1重量%を含む $\text{SiO}_2/\text{Al}_2\text{O}_3=25$ のβ-ゼオライト700部と、白金0.1重量%、ホウ素0.1重量%、カルシウム0.1重量%を含む $\text{SiO}_2/\text{Al}_2\text{O}_3=50$ のZSM5を100部と、リン0.5重量%、カルシウム0.1重量%を含む $\text{SiO}_2/\text{Al}_2\text{O}_3=25$ のUSY100部とを用いた以外は、実施例9に準じ、下流触媒Oを得た。

【0055】比較調製例1

$\text{SiO}_2/\text{Al}_2\text{O}_3=15$ のA型ゼオライト粉末900部と、シリカゾル(SiO_2 濃度として20%)500部とのみを用いた以外は、実施例1に準じ、上流触媒Pを得た。

【0056】比較調製例2

$[\text{La}_{0.6}\text{Sr}_{0.3}\text{Ba}_{0.1}][\text{Mn}_{0.4}\text{Co}_{0.4}\text{Fe}_{0.1}\text{Al}_{0.1}]\text{O}_x$ 粉末900部と、シリカゾル(SiO_2 濃度として20%)500部とのみを用いた以外は、実施例1に準じ、上流触媒Qを得た。

【0057】比較調製例3

パラジウム担持濃度0.1重量%のパラジウム担持セリウム酸化物($\text{La}_{0.01}\text{Zr}_{0.99}\text{Ce}_{0.99}\text{O}_x$)粉末900部と、シリカゾル(SiO_2 濃度として20%)500部とのみを用いた以外は、実施例1に準じ、上流触媒Rを得た。

【0058】比較調製例4

実施例2で得られた粉末B880g及び粉末D280gと、活性アルミナ40gと、硝酸水溶液1500gとを磁性ボールミルに投入し、混合・粉砕してスラリーを得た。このスラリー液をコーゼライト質モノリス担体(1.0L、400セル)に付着させ、空気流にてセル内の余剰のスラリーを除去・乾燥し、400℃で1時間焼成した。この作業を2度行い、コート量重量60g/L-担体の触媒を得た。パラジウム担持量は146.67g/cf(5.18g/L)であった(触媒S)。

【0059】次いで、実施例2で得られた粉末E470部と、La1モル%、Ce20モル%、Zr79モル%のジルコニウム酸化物粉末(粉末F)300部と、活性アルミナ30部と、硝酸水溶液1500gとを磁性ボールミルに投入し、混合・粉砕してスラリーを得た。このスラリー液を上記触媒Sに付着させ、空気流にてセル内の余剰のスラリーを除去・乾燥し、400℃で1時間焼成した。この作業を2度行い、コート量重量100g/L

L-担体の触媒を得た。ロジウム担持量は13.33 g/cf (0.47 g/L)であった(触媒T)。

【0060】次いで、上記触媒成分担持コーゼライト質モノリス担体に酢酸バリウム溶液を付着させた後、400℃で1時間焼成し、BaOとして10 g/Lを含有させて、下流触媒Uを得た。

【0061】比較調製例5

SiO₂/Al₂O₃=25のβ-ゼオライト粉末600部、SiO₂/Al₂O₃=50のZSM5 200部、SiO₂/Al₂O₃=25のUSY100部と、シリカゾル(SiO₂濃度として20%)を500部と、純水1500 gとを磁性ボールミルに投入し、混合・粉砕してスラリーを得た。このスラリー液を触媒Uに付着させ、空気流にてセル内の余剰のスラリーを除去・乾燥し、400℃で1時間焼成した。コート量重量300 g/L-担体の、下流触媒Vを得た。*

*【0062】比較調製例6

SiO₂/Al₂O₃=25のβ-ゼオライト粉末600部、SiO₂/Al₂O₃=50のZSM5 200部、SiO₂/Al₂O₃=25のUSY100部と、シリカゾル(SiO₂濃度として20%)を500部と、純水1500 gとを磁性ボールミルに投入し、混合・粉砕してスラリーを得た。このスラリー液を比較例4で得られた触媒Uに付着させ、空気流にてセル内の余剰のスラリーを除去・乾燥し、400℃で1時間焼成した。コート量重量200 g/L-担体の、下流触媒Wを得た。

【0063】上記調製例1～12及び比較調製例1～6で得られた各触媒の仕様を表1及び2に示す。

【0064】

【表1】

調製例	組成	コ-1量 (g/L)	PM量 (g/L)	備考
1 触媒A	SiO ₂ /Al ₂ O ₃ =15, A型C ₄ F ₆ [La _{0.85} Pr _{0.15} 0.1][Mn _{0.4} Cr _{0.6} 0.1Fe _{0.1} Mo _{0.1} 0.1]Cy Pd _{0.1} W _{0.1} La _{0.01} Zr _{0.02} Ce _{0.67} O ₃ SiO ₂ mol.	120.0 75.0 75.0 30.0	PM 0.075	触媒貯蔵・放出触媒
2 触媒E	SiO ₂ /Al ₂ O ₃ =25, B-C ₄ F ₆ SiO ₂ /Al ₂ O ₃ =50, 25MS SiO ₂ /Al ₂ O ₃ =25, C ₄ F ₆ SiO ₂ mol. Pd _{0.1} W _{0.1} Ce _{0.01} Zr _{0.02} La _{0.01} Al ₂ O ₃ Pd _{0.5} W _{0.1} La _{0.01} Zr _{0.02} Ce _{0.67} O ₃ Al ₂ O ₃ Rh _{0.2} W _{0.2} Zr _{0.01} Al ₂ O ₃ La _{0.01} Ce _{0.27} Pr _{0.72} O ₃ Al ₂ O ₃ H ₂ O	120.0 10.0 20.0 20.0 44.0 14.0 2.0 24.5 15.0 1.5 10.0	PM 5.18 PM 0.47	内層・ 炭化水素吸着材 中層・ 貴金屬成分層 外層・ 貴金屬成分層
3 触媒F	SiO ₂ /Al ₂ O ₃ =15, X型C ₄ F ₆ [La _{0.55} Pr _{0.45} 0.2]Ce _{0.05} Ni _{0.05}][Cr _{0.1} V _{0.03} W _{0.3} Fe _{0.1} Mo _{0.1} 0.05]Cy Pd _{0.1} W _{0.1} La _{0.01} Zr _{0.02} Ce _{0.67} O ₃ SiO ₂ mol.	170.0 75.0 75.0 30.0	PM 0.075	触媒貯蔵・放出触媒
4 触媒G	SiO ₂ /Al ₂ O ₃ =15, A型C ₄ F ₆ SiO ₂ /Al ₂ O ₃ =15, X型C ₄ F ₆ [La _{0.55} Pr _{0.45} 0.2]Ce _{0.05} Ni _{0.05}][Cr _{0.1} V _{0.03} W _{0.3} Fe _{0.1} Mo _{0.1} 0.05]Cy Pd _{0.1} W _{0.1} La _{0.01} Zr _{0.02} Ce _{0.67} O ₃ SiO ₂ mol.	30.0 30.0 30.0 150.0 30.0	PM 0.18	触媒貯蔵・放出触媒
5 触媒H	SiO ₂ /Al ₂ O ₃ =15, A型C ₄ F ₆ SiO ₂ /Al ₂ O ₃ =15, X型C ₄ F ₆ [La _{0.85} Pr _{0.15} 0.1][Mn _{0.4} Cr _{0.6} 0.1]Cy Pd _{0.1} W _{0.1} La _{0.01} Zr _{0.02} Ce _{0.67} O ₃ SiO ₂ mol.	15.0 15.0 30.0 210.0 30.0	PM 0.21	触媒貯蔵・放出触媒
6 触媒I	SiO ₂ /Al ₂ O ₃ =15, A型C ₄ F ₆ [La _{0.85} Pr _{0.15} 0.1][V _{0.03} Cr _{0.6} 0.1]Cy Pd _{0.1} W _{0.1} La _{0.01} Zr _{0.02} Ce _{0.67} O ₃ SiO ₂ mol.	15.0 15.0 240.0 30.0	PM 0.21	触媒貯蔵・放出触媒
7 触媒J	SiO ₂ /Al ₂ O ₃ =15, X型C ₄ F ₆ [La _{0.95} Pr _{0.05} 0.1][Co _{0.1} 0.1]Cy Pd _{0.1} W _{0.1} La _{0.01} Zr _{0.02} Ce _{0.67} O ₃ SiO ₂ mol.	15.0 15.0 240.0 30.0	PM 0.21	触媒貯蔵・放出触媒
8 触媒K	SiO ₂ /Al ₂ O ₃ =25, B-C ₄ F ₆ SiO ₂ /Al ₂ O ₃ =50, 25MS SiO ₂ /Al ₂ O ₃ =25, C ₄ F ₆ SiO ₂ mol. Pd _{0.1} W _{0.1} Ce _{0.01} Zr _{0.02} La _{0.01} Al ₂ O ₃ Pd _{0.5} W _{0.1} La _{0.01} Zr _{0.02} Ce _{0.67} O ₃ Al ₂ O ₃ Rh _{0.2} W _{0.2} Zr _{0.01} Al ₂ O ₃ La _{0.01} Ce _{0.27} Pr _{0.72} O ₃ Al ₂ O ₃ H ₂ O	160.0 10.0 10.0 20.0 44.0 14.0 2.0 24.5 15.0 1.5 10.0	PM 5.18 PM 0.47	内層・ 炭化水素吸着材 中層・ 貴金屬成分層 外層・ 貴金屬成分層
9 触媒L	SiO ₂ /Al ₂ O ₃ =50, B-C ₄ F ₆ SiO ₂ mol. Pd _{0.1} W _{0.1} Ce _{0.01} Zr _{0.02} La _{0.01} Al ₂ O ₃ Pd _{0.5} W _{0.1} La _{0.01} Zr _{0.02} Ce _{0.67} O ₃ Al ₂ O ₃ Rh _{0.2} W _{0.2} Zr _{0.01} Al ₂ O ₃ La _{0.01} Ce _{0.27} Pr _{0.72} O ₃ Al ₂ O ₃ H ₂ O	160.0 20.0 44.0 14.0 2.0 24.5 15.0 1.5 10.0	PM 5.18 PM 0.47	内層・ 炭化水素吸着材 中層・ 貴金屬成分層 外層・ 貴金屬成分層
10 触媒M	SiO ₂ /Al ₂ O ₃ =50, 25MS SiO ₂ /Al ₂ O ₃ =25, C ₄ F ₆ SiO ₂ mol. Pd _{0.1} W _{0.1} Ce _{0.01} Zr _{0.02} La _{0.01} Al ₂ O ₃ Pd _{0.5} W _{0.1} La _{0.01} Zr _{0.02} Ce _{0.67} O ₃ Al ₂ O ₃ Rh _{0.2} W _{0.2} Zr _{0.01} Al ₂ O ₃ La _{0.01} Ce _{0.27} Pr _{0.72} O ₃ Al ₂ O ₃ H ₂ O	60.0 100.0 20.0 44.0 14.0 2.0 24.5 15.0 1.5 10.0	PM 5.18 PM 0.47	内層・ 炭化水素吸着材 中層・ 貴金屬成分層 外層・ 貴金屬成分層

実施例	組成	コート量 (g/L)	PM量 (g/L)	備考
11 触媒H	SiO ₂ /Al ₂ O ₃ =50, Pd 5wt%, Cu 0.1wt%, β-セチレン SiO ₂ sol.	150.0		内層: 炭化水素吸着材
	Pd 11%, Ce 3mol%, Zr 3mol%, La 2mol%, Al ₂ O ₃ Pd 2.5%, La 0.01Zr 0.32Ce 0.67O _x Al ₂ O ₃	20.0 11.0 14.0 2.0	Pd 5.18	中間: 貴金属成分層
12 触媒O	Hf 2%, Zr 3wt%, Al ₂ O ₃ La 0.01Ce 0.22Zr 0.79O _x Al ₂ O ₃ BaO	23.5 15.0 1.5 10.0	Hf 0.17	外層: 貴金属成分層
比較 調製例	組成	コート量 (g/L)	PM量 (g/L)	備考
	SiO ₂ /Al ₂ O ₃ =15, A型セチレン SiO ₂ sol.	100.0 20.0 20.0 20.0		内層: 炭化水素吸着材
1 触媒P	[La 0.6Sr 0.3Ba 0.1][Vr 0.4Cu 0.4Fe 0.1Nb 0.1]O _y SiO ₂ sol.			中間: 貴金属成分層
	Pd 0.1%, La 0.01Zr 0.32Ce 0.67O _x SiO ₂ sol.			外層: 貴金属成分層
2 触媒Q	Pd 0.1%, Ce 3mol%, Zr 3mol%, La 2mol%, Al ₂ O ₃ Pd 2.5%, La 0.01Zr 0.32Ce 0.67O _x Al ₂ O ₃	11.0 11.0 14.0 2.0	Pd 5.18	中間: 貴金属成分層
	Hf 2%, Zr 3wt%, Al ₂ O ₃ La 0.01Ce 0.22Zr 0.79O _x Al ₂ O ₃ BaO	23.5 15.0 1.5 10.0	Hf 0.17	外層: 貴金属成分層
3 触媒R	SiO ₂ /Al ₂ O ₃ =25, Pd 1wt%, Ni 0.1wt%, Pt 0.1wt%, β-セチレン SiO ₂ /Al ₂ O ₃ =50, Pd 1%, Ba 0.1%, Cu 0.1%, γ-Si ₃ N ₄ SiO ₂ /Al ₂ O ₃ =25, Pd 0.5wt%, Cu 0.1wt%, γ-Si ₃ N ₄ SiO ₂ sol.	100.0 20.0 20.0 20.0		内層: 炭化水素吸着材
	Pd 11%, Ce 3mol%, Zr 3mol%, La 2mol%, Al ₂ O ₃ Pd 2.5%, La 0.01Zr 0.32Ce 0.67O _x Al ₂ O ₃	11.0 11.0 14.0 2.0	Pd 5.18	中間: 貴金属成分層
4 触媒U	Hf 2%, Zr 3wt%, Al ₂ O ₃ La 0.01Ce 0.22Zr 0.79O _x Al ₂ O ₃ BaO	23.5 15.0 1.5 10.0	Hf 0.17	外層: 貴金属成分層
	Pd 11%, Ce 3mol%, Zr 3mol%, La 2mol%, Al ₂ O ₃ Pd 2.5%, La 0.01Zr 0.32Ce 0.67O _x Al ₂ O ₃	11.0 11.0 14.0 2.0	Pd 5.18	中間: 貴金属成分層
5 触媒V	SiO ₂ /Al ₂ O ₃ =25, Pd 1wt%, Ni 0.1wt%, Pt 0.1wt%, β-セチレン SiO ₂ /Al ₂ O ₃ =50, Pd 1%, Ba 0.1%, Cu 0.1%, γ-Si ₃ N ₄ SiO ₂ /Al ₂ O ₃ =25, Pd 0.5wt%, Cu 0.1wt%, γ-Si ₃ N ₄ SiO ₂ sol.	100.0 20.0 20.0 20.0		内層: 炭化水素吸着材
	Pd 11%, Ce 3mol%, Zr 3mol%, La 2mol%, Al ₂ O ₃ Pd 2.5%, La 0.01Zr 0.32Ce 0.67O _x Al ₂ O ₃	11.0 11.0 14.0 2.0	Pd 5.18	中間: 貴金属成分層
6 触媒W	Hf 2%, Zr 3wt%, Al ₂ O ₃ La 0.01Ce 0.22Zr 0.79O _x Al ₂ O ₃ BaO	23.5 15.0 1.5 10.0	Hf 0.17	外層: 貴金属成分層
	SiO ₂ /Al ₂ O ₃ =25, β-セチレン SiO ₂ /Al ₂ O ₃ =50, γ-Si ₃ N ₄ SiO ₂ /Al ₂ O ₃ =25, γ-Si ₃ N ₄ SiO ₂ sol.	100.0 20.0 20.0 20.0		内層: 炭化水素吸着材

【0066】実施例1～12及び比較例1～7

* 触媒を、以下の耐久条件により耐久を行った。

前記調製例1～12及び比較調製例1～6で得られた各*

【0067】

耐久条件

エンジン排気量	3000cc
燃料	無鉛ガソリン
触媒入口ガス温度	500℃
耐久時間	50時間
入口ガス組成	CO 0.5±0.1% O ₂ 0.5±0.1% HC 約1100ppm NO 1300ppm CO ₂ 15%
A/F変動	2750回(周期65秒/回) 周期: A/F=14.6 55秒 燃料カット 5秒 リッチ スパイク 5秒(CO=2%)

【0068】次いで、耐久後の各触媒を、以下の表3に示す触媒配置及び図1に示す評価システムに設置して、排気ガス浄化用触媒装置を得た。各装置を用いて、排気*

* ガスを浄化する方法は以下の条件で行なった。

【0069】

浄化評価条件

エンジン排気量 日産自動車株式会社製 V型6気筒3.3L
燃料 無鉛ガソリン
評価モード LA4-CH (A-b a g)

【0070】各実施例、比較例について上記浄化条件で測定した評価結果(エミッション値)を表3に示す。脱離HC量は、上記コールドHC吸着量に対し、60秒

【0071】但し、コールドHC排出量は、触媒配置1にTWCを配置し、ベースエミッションを測定する。コールドHC吸着量は、触媒配置1にTWCを、配置2及び3に各々の触媒を配置し、上記ベースエミッション ※

【数1】

$$\text{脱離HC浄化率} = \frac{[\text{コールドHC吸着量}] - [\text{未浄化脱離HC量}]}{[\text{コールドHC吸着量}]} \times 100$$

脱離HC浄化量=コールドHC吸着量-未浄化脱離HC量として測定した。★【0072】

★ 【表3】

	触媒配置			コ-ルトHC 排出量 (g/test)	コ-ルトHC 吸着量 (g/test)	未浄化 脱離HC量 (g/test)	脱離HC 浄化率 (%)	脱離HC 浄化量 (g/test)
	1	2	3					
実施例 1	TWC	触媒A	触媒E	1.22	0.915	0.706	22.8	0.209
実施例 2	TWC	触媒F	触媒E	1.22	0.915	0.705	23.0	0.210
実施例 3	TWC	触媒G	触媒E	1.22	0.915	0.704	23.1	0.211
実施例 4	TWC	触媒H	触媒E	1.22	0.915	0.702	23.3	0.213
実施例 5	TWC	触媒I	触媒E	1.22	0.915	0.703	23.2	0.212
実施例 6	TWC	触媒J	触媒E	1.22	0.915	0.700	23.5	0.215
実施例 7	TWC	触媒A	触媒K	1.22	0.927	0.708	23.6	0.219
実施例 8	TWC	触媒F	触媒L	1.22	0.939	0.719	23.4	0.220
実施例 9	TWC	触媒G	触媒M	1.22	0.903	0.693	24.4	0.220
実施例 10	TWC	触媒H	触媒N	1.22	0.939	0.718	23.5	0.221
実施例 11	TWC	触媒I	触媒O	1.22	0.952	0.731	23.2	0.221
実施例 12	TWC	触媒J	触媒E	1.22	0.915	0.698	23.9	0.219
比較例 1	TWC	なし	触媒E	1.22	0.915	0.714	22.0	0.201
比較例 2	TWC	触媒P	触媒E	1.22	0.915	0.715	21.9	0.200
比較例 3	TWC	触媒Q	触媒E	1.22	0.915	0.715	21.9	0.200
比較例 4	TWC	触媒R	触媒E	1.22	0.915	0.713	22.0	0.202
比較例 5	TWC	触媒A	触媒U	1.22	0.915	0.910	0.55	0.005
比較例 6	TWC	触媒A	触媒V	1.22	0.915	0.759	17.0	0.156
比較例 7	TWC	触媒A	触媒W	1.22	0.915	0.915	0.000	0.000

【0073】

【発明の効果】請求項1記載の排気ガス浄化方法は、酸素貯蔵・放出能を有す触媒と炭化水素吸着・浄化能を有する触媒とを組み合わせ、内燃機関から排出されるエンジン始動直後の低温排気ガス中の炭化水素を吸着した触媒が触媒層温度の上昇によって炭化水素を脱離する際に浄化に必要な酸素を供給することによって、炭化水素の浄化性能を向上し、未浄化のまま排出される炭化水素を大幅に低減させることができる。

【0074】請求項2記載の排気ガス浄化方法は、上記

効果に加えて、酸素吸着材として $\text{SiO}_2/\text{Al}_2\text{O}_3$ 比が20以下のA型及びX型ゼオライトを用いることによって、触媒層の温度変化で酸素の選択的に分離・吸着との放出を容易に制御でき、炭化水素を吸着した触媒層温度の上昇によって炭化水素を脱離する際に、浄化に必要な酸素を供給でき、浄化性能を向上することができる。

【0075】請求項3記載の排気ガス浄化方法は、上記効果に加えて、酸素吸着材として用いるゼオライトが熟によって破壊されるのを抑制でき、該ゼオライトが酸素

を分離・吸着・放出する性能の維持を図ることができる。

【0076】請求項4記載の排気ガス浄化方法は、上記効果に加えて、耐熱性が高く酸素移動性の高い材料を含有することによって、該触媒が酸素を分離・吸着する性能の向上を図ることができる。

【0077】請求項5記載の排気ガス浄化方法は、上記効果に加えて、該触媒が酸素を放出する性能の向上を図ることができる。

【0078】請求項6記載の排気ガス浄化方法は、上記効果に加えて、種々の炭化水素吸着材を組み合わせることにより、エンジン始動直後の低温時に排出される炭化水素種を高い効率で吸着し、しかも、貴金属成分を炭化水素吸着材と接触することで脱離する炭化水素の浄化能を向上できる。

【0079】請求項7記載の排気ガス浄化方法は、上記*

*効果に加えて、エンジン始動直後の低温時に排出されるHC種を高い効率で吸着し、しかも、耐久後の構造変化や性能劣化が小さいため、脱離速度の遅延化を図ることができる。

【0080】請求項8記載の排気ガス浄化方法は、上記効果に加えて、触媒成分の還元に起因する触媒性能の低下を抑制できる。

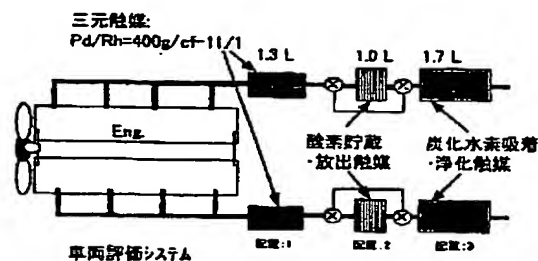
【0081】請求項9記載の排気ガス浄化方法は、上記効果に加えて、更に浄化性能を向上し、触媒成分の被毒に起因する触媒性能の低下を抑制できる。

【0082】請求項10記載の排気ガス浄化方法は、上記効果に加えて、パラジウムの低温活性を向上し、更に、シンタリング抑制し耐久性を向上できる。

【図面の簡単な説明】

【図1】本発明の排気ガス浄化方法を有効に実施する評価システムの一例を示す概略図である。

【図1】



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(72) 発明者 都筑 幹雄
神奈川県横浜市神奈川区宝町2番地 日産
自動車株式会社内

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